WL-TR-93-2033

SCHOLARLY RESEARCH PROGRAM IN FUEL ANALYSIS AND COMBUSTION RESEARCH

University of Dayton Research Institute
300 College Park Avenue, KL 102
Dayton, Ohio 45469-0132

February 1993

Final Report for Period September 1987 - September 1992

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AERO PROPULSION AND POWER DIRECTORATE
WRIGHT LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-7650

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This technical report has been reviewed and is approved for publication.

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13. ABSTRACT *(Maximum 200 words)*

A total of 40 individually funded tasks were performed under this effort. These tasks were concerned with many fuel analysis and combustion research, conducted for the Fuels Branch (WL/POSF), Lubrications Branch (WL/POSL) and other Aero Propulsion and Power Directorate Laboratories. This report is a compilation of 1-2 page summaries from each of the tasks. More information on each task is available in the technical reports, journal articles, letter reports or informal information listed for the project. Although the subjects covered under this contract are too varied to list here, the most often addressed areas were research topics in gas chromatography and related instrumentation, thermal stability testing and methods development, lubrications research and combustion studies.

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FOREWORD

This report was prepared by the Environmental Sciences Group of the University of Dayton Research Institute, Dayton, Ohio. It represents a collection of research programs, varying broadly in size and complexity with many authors and principal investigators. The tasks associated with this contract, numbered from Task 1 to Task 42, are summarized in this final report. Each individual task may have associated with it a final report which may be a University of Dayton report, an Air Force Technical Report or merely compilations of technical information. This report, along with its attachments and associated technical reports, describes all of the work conducted under the subject contract.

This effort was performed under contract F33615-87-C-2714 for the Fuels Research Group (WL/POSF) of the Aero Propulsion and Power Directorate of Wright Laboratory, Air Force Materiel Command. The authors wish to acknowledge the efforts of Mr. Steven D. Anderson, who was the project technical monitor throughout the length of the contract. His technical and administrative direction was essential in the successful completion of this very complex task order contract.

The authors also wish to acknowledge the efforts of members of the University of Dayton who were principal investigators for various tasks in the contract: Ms. Sue L. Mazer, Dr. Costy Saba, Dr. L. Krishnamurthy, Mr. Nathan Vonada, Dr. Perry Yaney, Mr. Edward Binns, Dr. Binod Kumar, Mr. Robert Kauffman, Mr. Douglas Wolfe, Mr. Wayne Rubey, Mr. Richard Striebich, and others. We also recognize the efforts of the investigators from other subcontracted studies. Finally, we commend the Contracts and Grants Administration staff (Ms. Claudette Spanel and Ms. Carol Eckley) for their efforts in procuring and handling 42 separate internal and external research tasks.

SECTION 1. SUMMARY

This report is only meant to be a compilation of the most general information about a particular research project conducted under this task order contract. More information about the project is available in the List of Reports for the tasks as specified in Section 4.

There were at least 34 publications for the 40 tasks which comprised this project. These publications included final reports, University of Dayton reports, US Air Force Technical reports, and subcontractor reports, as well as journal articles. This collection of research represents a tremendous effort in the areas of fuels analysis and combustion.

SECTION 2. INTRODUCTION

In the mid-1980s, Project Forecast II identified technologies that the Air Force would like to pursue into the twenty-first century. Among these technologies were certain propulsion related topics, such as fuels and combustion systems for high altitude, high mach aircraft. Supersonic and hypersonic aircraft (as envisioned for the National Aerospace Plane or the Transatmospheric Vehicle) may employ either air turbo-ramjet or scramjet engines to reach speeds of Mach 3 to Mach 25. The severe conditions generated due to aerodynamic heating at these high speeds will necessitate the development of specially designed fuels, combustors, lubricants, hydraulic fluids, composites and sealants.

Although the final product of a National Aerospace Plane is a long range objective, trends in the development of new aircraft are also reflecting the development of fuels and combustion systems that can accept higher heat loads. The Advanced Tactical Fighter represents an increase in overall heat load as compared to current systems (see Figure 1) and the Integrated High Performance Turbine Engine Technology represents another major advance in capability. The movement from current baseline fuels and combustion systems is shown in Figure 2. In order to obtain these higher capability engines and aircraft, research and development of advanced fuels and combustion systems is a great necessity.

The purpose of this effort was to investigate individually assigned tasks in the general research areas of thermal stability, jet fuel development and fuel combustion. These tasks could be assigned and addressed quickly in case of urgent problems which required immediate attention. Also, tasks assigned may have been too small for normal contracting procedures such as addressing a current or proposed approach. This effort was also used to define or explore possible solutions to more complex technical issues.

Under this contract, the principal investigator was assigned from either the University of Dayton Research Institute (UDRI) or, if significant expertise did not exist within the UDRI, from other contracted experts outside the University. This arrangement ensured that work could be addressed by a wide variety of researchers, with an emphasis on quality, quick-response research.

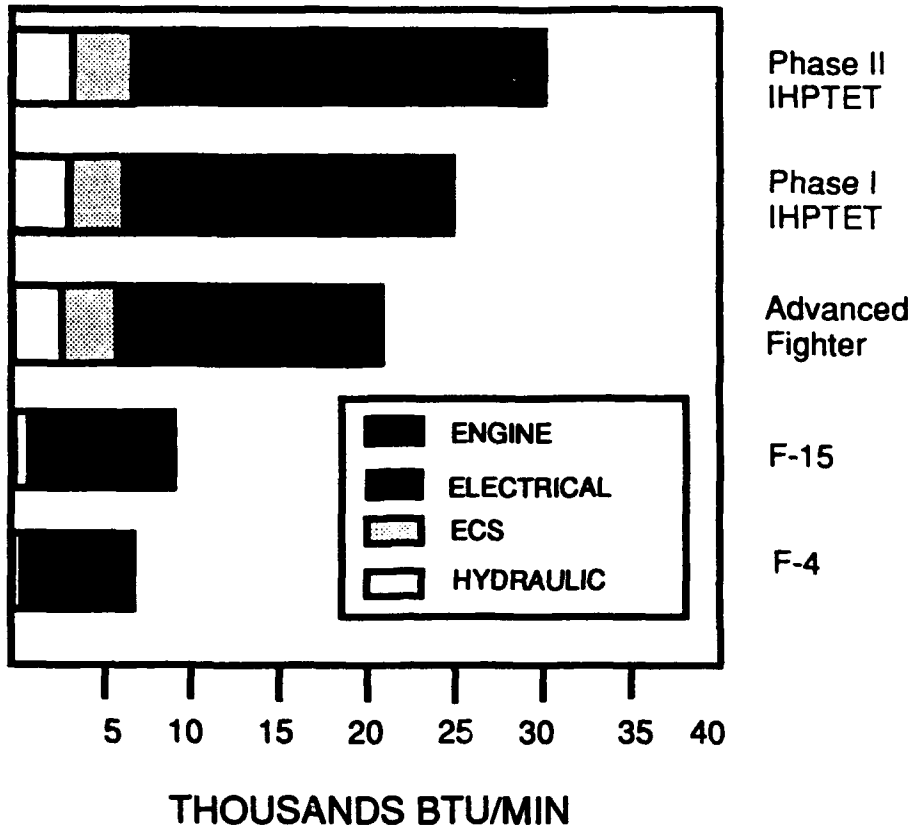

Figure 1. Heat Loads for Various Aircraft.

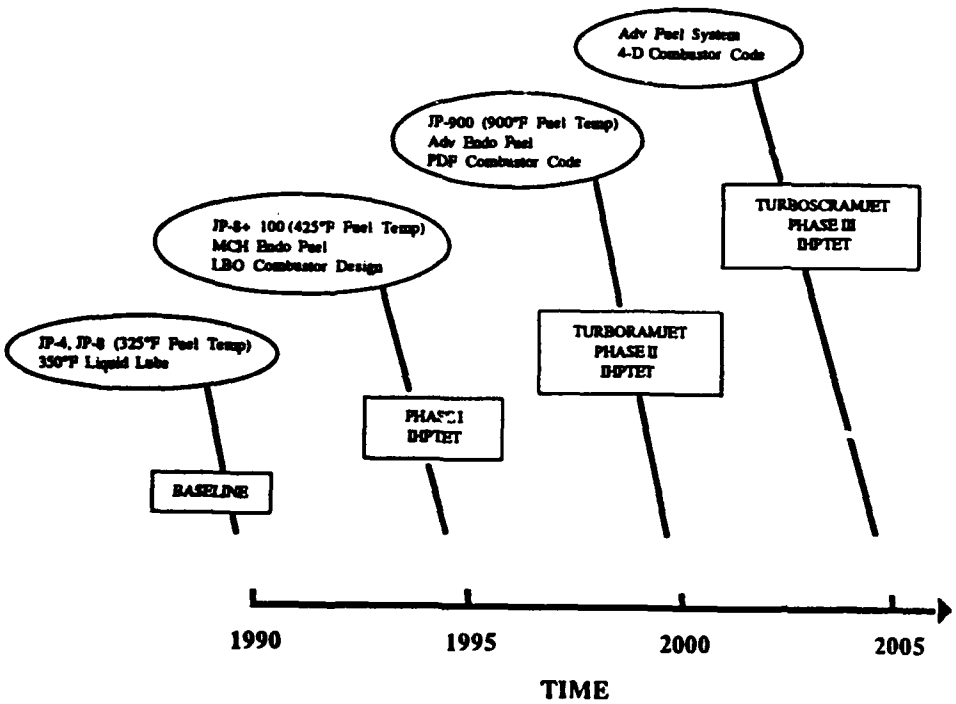

Figure 2. Advanced Fuels and Combustion Goals.

SECTION 3. TASK DESCRIPTIONS AND SUMMARIES OF RESULTS

The following sections are brief descriptions of the tasks assigned under this program. These descriptions include information about the principal investigator and their affiliation, the program duration and other general information about the task. These descriptions also include a brief summary of the product of the task, which may be a research finding, the development of an instrumentation system or literature review. In many tasks, there were reports and informal technical information generated as a result of this effort. These reports are cited whenever possible.

The task numbers follow in logical, numerical order with a few exceptions. Tasks 8, 10, 11 and 24 were tasks which were cancelled by the government due to lack of funding or change in program interest. Tasks 9b and 31a represent additional funding added to Tasks 9 and 31 to cover an increase in the scope of each task.

Task: 01
Title: Mass Spectrometry Short Course
Principal Investigator: Ms. Sue L. Mazer
Affiliation: Hewlett Packard Company, Palo Alto, CA
Start/Stop Dates: 20 September 1987 - 4 December 1987

Reports or Technical Information Generated:
Customized GC-MS Training: Course Notes (200 pages)
Mass Spectral Interpretation Notes (100 pages)

Task Description:

Gas Chromatography-Mass Spectroscopy (GC-MS) is one of the most powerful analytical techniques available for the identification of complex mixtures of organic materials. This technique is currently being employed at the Fuels Laboratory (WL/POSF) for the identification of individual components of complex hydrocarbon fuels. If individual components of current and future fuels can be identified, then it may be possible to determine which components influence which properties of jet fuels. With this knowledge, better jet fuels can be designed for specific applications and needs.

The GC-MS system used at WPAFB is a Hewlett-Packard (HP) Gas Chromatograph with Mass Selective Detection (GC-MSD). The WL/POSF personnel operating this instrument needed to be trained in the operation, data reduction capabilities and troubleshooting of the GC-MSD system. In addition, there was a great need to train personnel in the interpretation of mass spectral information specifically for current and future jet fuels.

Course Description:

A customized mass spectral training course was presented for researchers at WL/POSF. This course was 40 hours duration and included instruction on operation of the in-house HP 5890 GC/HP 5970 MSD systems, use of the full capabilities of the data station software, interpretation of mass spectra, and writing of automated data reduction programs (MACROs). Examples specifically relevant to analyses of existing and future jet fuels were presented throughout the course.

This course was about 50% lecture and discussion and 50% hands-on operation of the GC-MS data system. The hands-on operation was performed using the existing GC-MSD-workstation system in the Fuels Lab, as well as a second workstation which was provided by UDRI for the duration of the course. This second system enabled more hands-on interaction and also illustrated some of the additional capabilities of the latest version of software available for the workstation. In addition to actual

workstation practice, course participants were given the opportunity to interpret mass spectra in several "dry labs." The objectives of the course were as follows:

1. Each participant was to be able to use the GC-MSD to properly analyze samples and reduce the data.

2. Each participant was to understand and apply the fundamentals of mass spectral interpretation.

3. Customized MACROs and reporting formats were established on the on-site system, which enabled automated and overnight data reductions.

Summary of results:

The GC-MS course was given from 30 November 87 - 4 December 87. There were five researchers from WL/POSF participating in the course. Some 300 pages of class notes and reference materials were distributed for the course. The course outline was as follows:

1/2 day I. GC-MSD: Theory and Practice
- A. Familiar ground: GC, sample prep
- B. GC-MS interfaces
- C. The mass spectrometer
  1. Sample ionization - electron impact
  2. Mass separation - quadrupole operation
  3. Ion detection - electron multiplier

1-1/2 days II. GC-MSD Workstation Operation
- A. Tuning
- B. Data acquisition
- C. Data reduction - data editor
- D. Report generation
- E. Utilities and file management
- F. Text editor
- G. Sequencing and use of autosampler
- H. Troubleshooting

2 days III. Mass Spectral Interpretation

A. Hydrocarbons

B. Heteroatom-containing compounds likely to be present in fuels

C. Other compounds - common analysis contaminants

1 day IV. MACRO Writing for Automated Data Reduction

A. Introduction to MACROs

B. RPN commands used in MACROs

C. Creating and using "standard" MACROs

D. Creating and using customized MACROs

Task: 02

Title: Development of a System for Thermal Degradation Studies of Advanced Fluids

Principal Investigators: Mr. Wayne A. Rubey and Mr. Richard C. Striebich

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start/Stop Dates: 1 April 1988 - 30 November 1989

Reports or Technical Information Generated:

W. A. Rubey and R. C. Striebich, A System for Thermal Diagnostic Studies (STDS); Description and Operation, UDR-DR-89-15, April 1989

W. A. Rubey and R. C. Striebich, A Tubular Gas Flow Reactor Test Cell Assembly: Description-Operation-UDR-DR-89-16

Task Description:

Liquid organic lubricants were needed which could function at temperatures greater than 600°F, and some special lubricant mechanisms were considered which could withstand temperatures as high as 1600°F. It was anticipated that the various liquid organics would contact a variety of hot metal surfaces which could also impact their chemical stability.

The evaluation of various candidate high-temperature lubricants needed to be examined for their thermal stability and associated thermal degradation behavior. Specifically, it was of key importance to determine those physiochemical conditions that initiate the onset of thermal degradation. Also, the chemical nature of the various thermal decomposition products formed were of interest.

A System for Thermal Diagnostic Studies (STDS) was designed and assembled to address a broad range of both lubricant materials and hydraulic fluids. Before delivering this system, UDRI demonstrated that high temperature lubricants, such as polyphenylether lubricants (5P4E), could be efficiently transported through the STDS while in the gas phase. Provisions were made in this system for the incorporation of solid samples of lubricants that may be tested. The ability of the STDS to incorporate a pyroprobe assembly was demonstrated. The pyroprobe can be used to volatilize certain components from solid lubricants and ascertain the composition of these volatiles using GC-MS-FTIR.

This instrumentation assembly was designed for analyses of a wide range of sample types, atmospheric conditions, residence times and exposure temperatures. The ability to investigate thermal decomposition of lubricants materials at temperatures up to 1050°C was demonstrated by the degradation of a polyphenylether lubricant over the STDS entire range of temperatures. The STDS was demonstrated

to be operated in such a manner as to conduct fundamental reaction kinetic and thermodynamic studies, which could be invoked to assist in the evaluation of various high temperature lubricant candidates.

The ability of the system to conduct experiments over a wide range of gaseous oxygen concentrations was demonstrated. The STDS mainframe assembly was especially sensitive with respect to effluent analysis. High-resolution gas chromatography was applied primarily for the evaluation of the thermal decomposition behavior of these lubricant candidates. It was demonstrated that GC-MS-FTIR can be incorporated into the STDS; this analytical capability allows unsurpassed ability to separate and identify thermal reaction products in the gas phase. The flame ionization detector was used on this system when mass spectral identification was not required.

Summary of Results:

UDRI designed, constructed and delivered a System for Thermal Diagnostic Studies (STDS) to the Lubrications Branch in November 1989. A complete description of the system is available in two reports which are manuals for the system. The titles of these reports are provided above.

The proper operation of the system was verified by examining the thermal decomposition of the 5P4E (polyphenylether) lubricant under various oxidative and pyrolytic conditions (see Figure 3). Mr. Edward Pitzer, WL/POSL was trained in the operation and maintenance of the system.

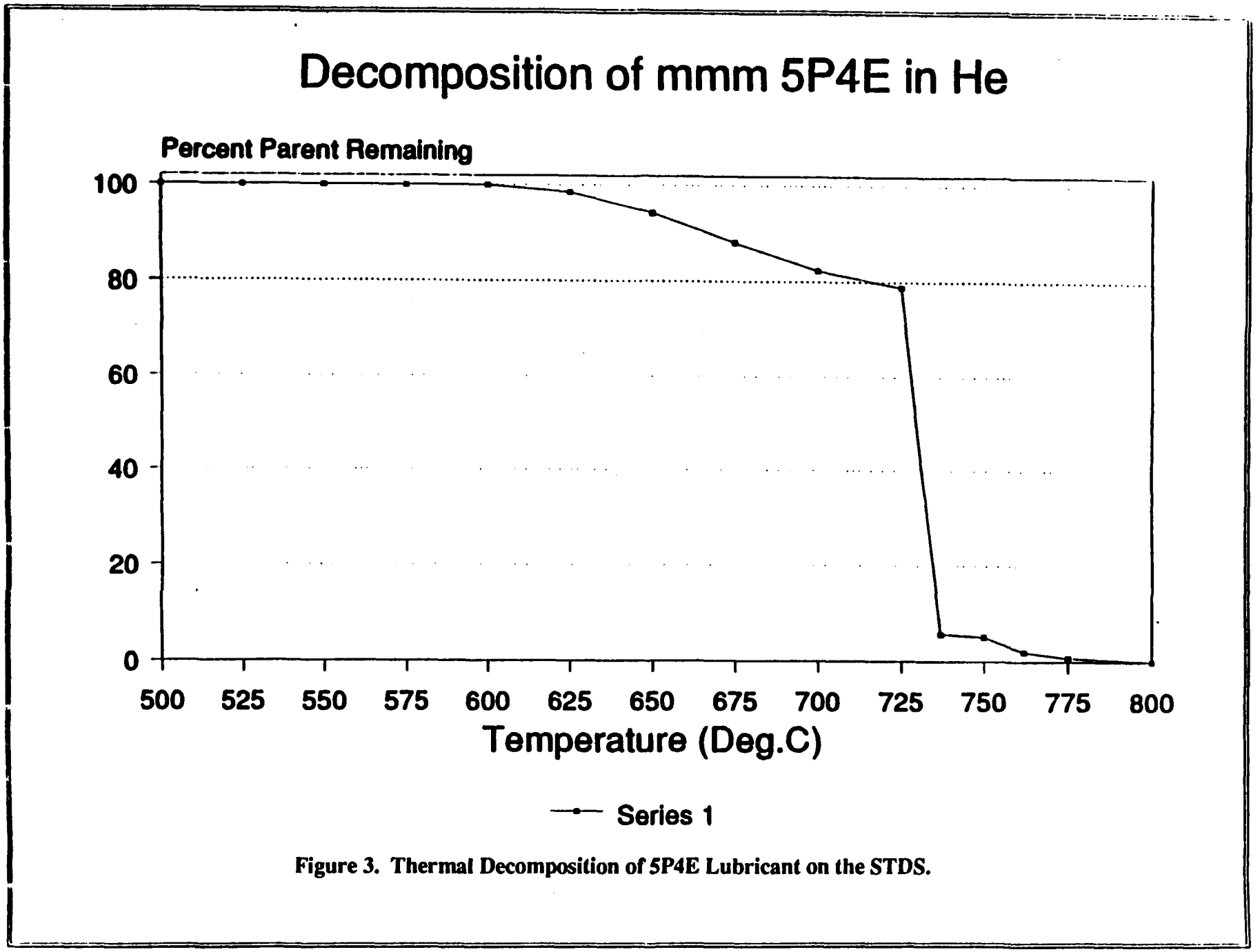

Figure 3. Thermal Decomposition of 5P4E Lubricant on the STDS.

Task: 03

Title: Low Pressure Microreactor Test Cell Assembly for the System for Thermal Diagnostic Studies (STDS)

Principal Investigator: Mr. Richard C. Striebich

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start/Stop Dates: July 1988 - December 1989

Reports or Technical Information Generated:

R. C. Striebich, Low Pressure Catalytic Test Cell Assembly, UDR-TR-91-99;

Related Documents: J. R. McCoy, Studies on the Mechanism of Olefin Metathesis Promoted by a Rhenium Oxide - Alumina Catalyst, in partial fulfillment of the requirements for a Ph.D., January 1991

Task Description:

The products of thermal reaction are quite important to the concept of the endothermic fuel. If heat is dissipated through endothermic reactions and the reaction products produced are low-energy content materials, the combustion process which follows the endothermic reactions will suffer. In short, the products of the endothermic reactions must, themselves, be an acceptable fuel for the combustion process. Thus, catalyst candidates need to be investigated to not only maximize the amount of heat dissipated in endothermic reactions, but also to identify what kind of products are being produced from the endothermic reaction.

In addition, basic experiments in catalytic activity and product formation must be conducted in order to direct research to an appropriate end product. Catalytic experiments, using well controlled thermal instrumentation, provide relevant information about the activity and selectivity of certain catalyst candidates. The ability to use small amounts of sample and catalyst is important in order to quickly and efficiently examine a number of catalyst candidates.

A test cell assembly was designed and constructed to investigate the activity and selectivity of various catalyst candidates. This test cell assembly was versatile enough to address a number of different catalyst geometries, such as a "honeycomb" type catalyst, a precious metal loaded onto a catalyst support, or an open-tubular arrangement of a metal coated on the wall of the quartz tube.

In addition to the test cell itself, the analysis techniques associated with the experiments conducted were given a great deal of consideration. Low molecular weight compounds were frequently the products of interest from these catalytic experiments and were difficult to analyze in this

configuration. Chromatographic columns had to be carefully chosen in order to address a wide range of reaction products of interest.

With these concerns in mind, a test cell assembly analyzed both low and high molecular weight materials while still incorporating the Mass Selective Detector.

Summary of Results:

A laboratory flow reactor system was constructed to conduct pulsed micro reactor experiments on very small amounts of catalyst. The reactor for this system contained a catalyst bed which could be calcined repeatedly with air and then used to conduct experiments in a helium atmosphere. The design incorporated in-line gas chromatography-mass spectrometry (GC-MS) to identify products formed from the gas phase catalytic reactions.

Pulsed experiments conducted with 1-pentene showed product formation as seen in Figure 4. This work also represents one of the first applications of "on-the-fly" mass spectrometry for light gas formation, which has been used in many subsequent STDS-type experiments.

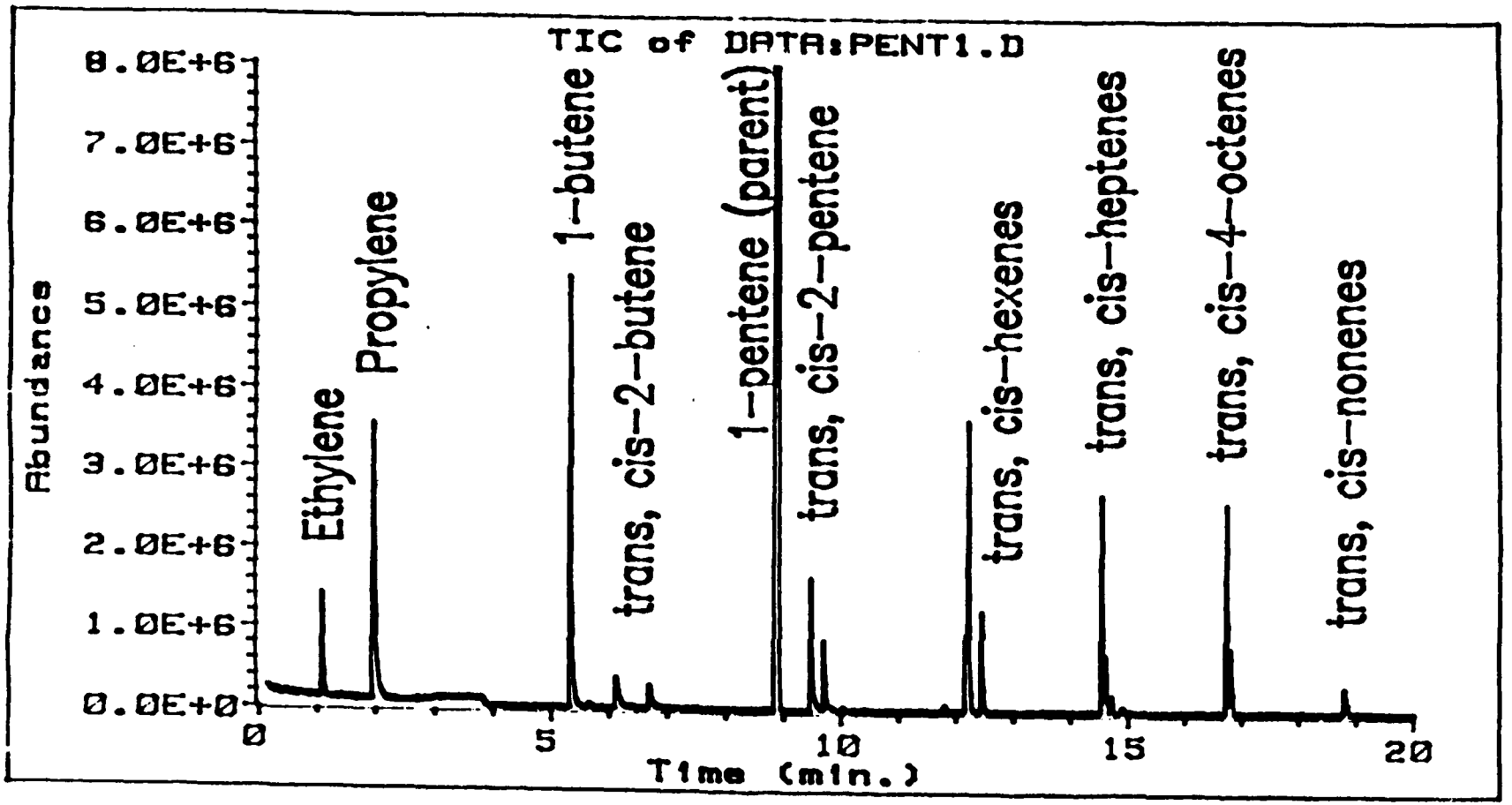

Figure 4. 1-Pentene Injection Into an Active Catalyst.

Task: 04
Title: Alternate Spectrometric Oil Analysis Techniques
Principal Investigator: Dr. Costy Saba
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: 1 October 1988 - 31 December 1990

Reports or Technical Information Generated:
Various Status Reports and Informal Technical Information.

Task Description:

Due to different types and degrees of wear, generated wear metal particles may ranged from submicron to millimeters in size. Since B_3 200 filters proved to retain particles greater than 3 micron and greatly reduce metal content in used oil samples, lubrication systems using microfiltration required instruments having higher sensitivity for wear metals with sub-ppm detection limits. Evaluation required comparative analysis using spectrometers presently used by the tri-services and other methods such as the acid dissolution method (ADM), inductively coupled plasma (ICP) spectrometry, and the graphite furnace. Used oil samples from operational lubrication systems using microfiltration and samples generated from the microfiltration test rig were used for this investigation. This combined effort (Army, Navy, Air Force) enhanced the overall joint oil analysis program (JOAP) in efficient detection of incipient engine failure.

Thus, by monitoring used engine oils for various properties, the goal of this program was to predict engine failure for operational aircraft.

Summary of Results:

The microfiltration test rig and membrane filtering techniques were completed. Approximately 80 used oil samples were generated from this work including pre- and post-filtered samples. A total of 274 oil samples were analyzed using ICP, AE, AA and other spectrometric techniques. About half the samples were SOAP samples from operational engines, one-third from the microfiltration testing and the rest were "old" field samples from a previous program. In addition to instrumental analyses, work performed included improving the ICP sample introduction system, determining the conditions which are necessary for overloading the ICP source, choosing an optimum dilution solvent for ICP and investigating the impact of analysis of wear debris in mineral oils in relation to the selection of analytical wavelengths. Even though many types of samples were analyzed, the "real" samples from operational engines were taken at random and at different times since oil change. The data collected to date do not provide information for developing wear metal trends using the ICP or other analytical techniques. Therefore, a

recommendation was made for extending this part of the program under "no cost time extension" for a period of at least 6 months so that a meaningful evaluation of the ICP spectrometer with respect to wear metal trending can be performed on "real" samples from several engines that are and are not presently monitored by SOAP.

Since the last quarterly report, 12 "SOAP" samples have been received from 6 operational engines. Only two engines were sampled twice. The ICP data for these engines are not sufficient to provide wear metal trends unless more samples are received.

Presently, a comprehensive final technical report is being finalized. The report will include all analytical data, data analysis conclusions, recommendations and rationale.

Task: 05

Title: Development of Test Cell Assemblies for the STDS: High Pressure Cell and Catalytic High Pressure Cell

Principal Investigator: Mr. Richard C. Striebich

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start-Stop Dates: July 1988 - May 1990

Reports or Technical Information Generated:

R. C. Striebich and W. A. Rubey, A Condensed Phase Test Cell Assembly for the System for Thermal Diagnostic Studies, WL-TR-92-2040, August 1992. Work for this report also conducted under F33615-90-C-2047

Task Description:

This research activity was directed at developing test cell assemblies to be used on the System for Thermal Diagnostic Studies (STDS) which is located at WL/POSF (Fuels Branch) at Wright Patterson Air Force Base.

A "Condensed Phase Test Cell" (CPTC) was designed to investigate the thermal degradation of liquid phase and mixed gas and liquid phase materials under higher temperatures and pressures than currently done in gas phase experiments.

Summary of Results:

A reactor and its associated peripherals was designed to be an integral part of the System for Thermal Diagnostic Studies (STDS), a versatile mainframe thermal system. The Condensed Phase Test Cell (CPTC) was used to conduct experiments for flowing liquids at temperatures up to approximately 800°C and pressures up to 1500 psig. In the area of thermal stability, the CPTC was used to conduct flowing experiments on jet fuels, jet fuel candidates and model mixtures at both subcritical and supercritical conditions. By subjecting condensed phase liquids to controlled conditions of temperature, pressures, reactive atmosphere (dissolved oxygen concentration) residence time and residence time distribution, etc., thermal degradation experiments could be conducted. Product distributions from the exposure of liquid phase and condensed phase material were performed, via high pressure liquid sampling valves, in line with gas chromatography-mass spectrometry (GC-MS). This technique was capable of measuring dissolved fixed gases (nitrogen, oxygen, argon, carbon dioxide, etc.), cracked gases (methane, ethane, ethylene, propylene, etc.) and thermal reaction products of the parent material (see Figure 5). The system was also designed to perform in-line extraction of deposits from the reactor using supercritical CO_2. Results indicated pyrolysis and autoxidation mechanisms were taking place at various

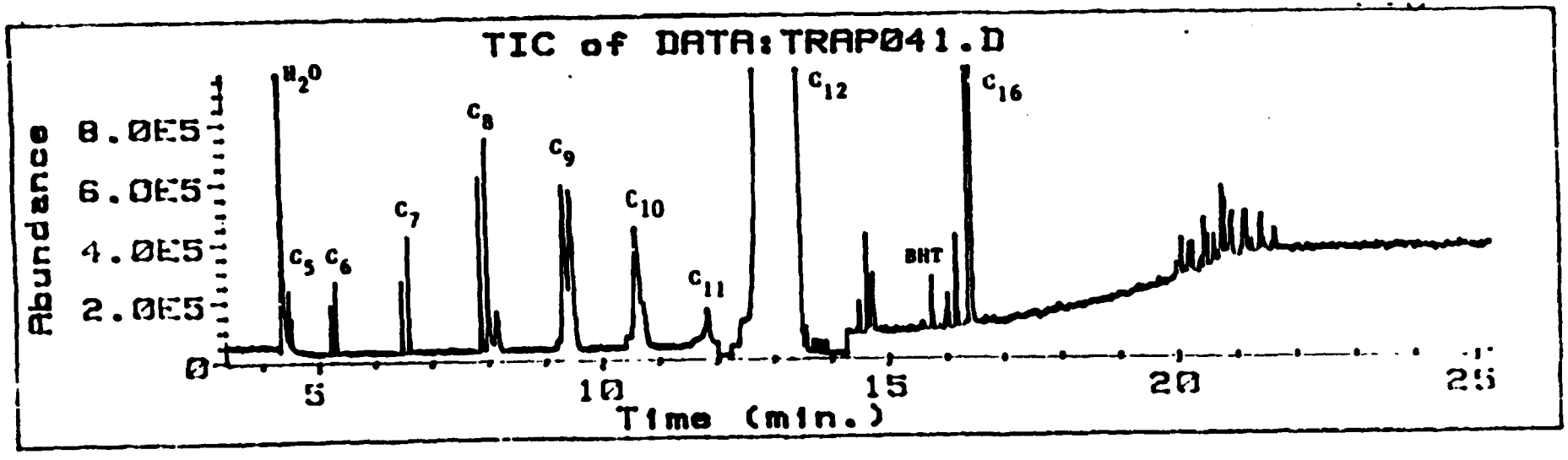

Figure 5. Thermal Degradation of Dodecane, Hexadecane and BHT at 480°C and 500 psi.

temperatures and conditions affecting product formation. Reaction products were identified which may be precursors to deposit formation.

Task: 06
Title: Laboratory Softwware Installation and Training
Principal Investigator: Mr. Nathan Vonada
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: March 1989 - April 1990

Reports or Technical Information Generated:
Informal procedures for transferring data from lab instruments to mainframe computer systems

Task Description:

The Fuels Research Group (WL/POSF) at Wright Patterson AFB performs analyses of jet fuels by various methods of analytical chemistry including gas chromatography, liquid chromatography, elemental analysis, etc. The goal of this analysis was to identify as many of the jet fuel constituents as possible. After accumulating this data for a number of samples, computer routines are typically developed to try to relate this compositional data to aircraft engine performance data such as smoke point, luminometer number, combustion efficiency and other measures of engine performance.

The preparation of these computer routines and the linking of analytical instrumentation with mainframe computers were the subject of this particular scholarly research task. Personal computers were necessary to upload data to larger computers and to prepare and manipulate data and software for incorporation onto larger computer systems.

Summary of Results:

Mr. Nathan Vonada was responsible for installing and debugging chromatographic software which had been purchased to perform statistical routines for projects such as those described above. This individual had to understand the computer operating systems and also have a knowledge of the specific instruments located in the laboratory in order to fully integrate these activities in a timely fashion. Mr. Vonada worked on-site at the Fuels and Lubrications Division in an instructional capacity to integrate all existing and new computational concepts. Duties performed included installing software on various computers, check-out and debugging as necessary, and training the government employees on commands and procedures. In addition, operating the laboratory analytical instruments on an intermittent basis was necessary to ensure that all potential computational capabilities were being fully exploited.

This individual also prepared operating instructions for using the software and computer systems he operated. These instructions reside on the Microvax as "interactive help commands."

Task: 07
Title: Turbulence Modeling
Principal Investigator: Dr. L. Krishnamurthy
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: February 1989 - August 1989

Reports or Technical Information Generated:
L. Krishnamurthy, Sensitivity Development for the K-E Turbulence Model, UDR-TR-89-36, May 1989

Task Description:

The subject research is of interest in the context of the ongoing experimental and computational fluid dynamic (CFD) dump-combustor investigation at the Air Force Wright Aeronautical Laboratories, Aero Propulsion Laboratory (AFWAL/POPT). In-house investigations have observed significant differences between the experimental measurements and the CFD predictions based upon the Reynolds-averaged Navier-Stokes equations and the k-ε turbulence model, thereby suggesting that the current CFD approaches do not provide sufficiently accurate predictions of confined, swirling, recirculating flowfields. This research addressed the examination of inverse-problem approaches, with the view to arriving at optimal k-ε for the dump-combustor configuration through the use of available experimental data in conjunction with sensitivity analysis and variational techniques.

Summary of Results:

During the subject task, the following research areas were addressed:

- Completion of the development of the sensitivity equations.
- Development of appropriate inverse-problem approaches (which involved variational techniques) for the application of experimental data to the sensitivity equations.
- Examination of the k-ε model equations, with special emphasis on the pressure velocity- and triple-velocity -correlation terms.
- Investigation of issues relating the numerical techniques for solving the sensitivity equations and the implementation of the numerical algorithms in the machine computation with the FLANELS-2D code. It is emphasized here that these aspects had to be addressed since the optimization of the turbulence model by means of the sensitivity analysis strongly depends on the access to, and the familiarity with, the FLANELS code. Actual programming of the sensitivity equations and computational fluid dynamic investigations were not addressed during

this task. A follow-on program would be required to address the programming of the equations and the implementation in the FLANELS code, computational case studies, and model optimizations.

Task: 09, 9b
Title: Computer Upgrade for the STDS
Principal Investigator: Mr. Richard C. Striebich
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: May 1989 - December 1989

Reports or Technical Information Generated:
Documentation on the Laboratory VAX Computer

Task Description:

The STDS is capable of taking mass spectrometric data from its own computer workstation; however, in order to take flame ionization detector data (FID data), the STDS uses a small stand-alone integrator made by Hewlett-Packard. This integrator is not capable of storing more than one chromatographic file or of archiving the files in any way. In addition, the Fuels Branch has a good deal of internally developed and commercially purchased software at its disposal on a DEC Microvax II computer. In order to utilize all of this software in the most efficient manner possible, it was desirable to configure the STDS to be controlled directly from the Microvax computer. This had to include the control of method development and sequencing on the analytical instrumentation, as well as data manipulation in the post-analysis mode.

It was desirable to allow chromatographic files to be transferred from existing Hewlett Packard systems to the Microvax II in order to take advantage of sophisticated computer software for existing STDS data. This upgrade of the STDS gave the system a great deal more flexibility and power in accumulating and processing chromatographic data.

Summary of Results:

In order to upgrade the STDS, we purchased both computer software and hardware to conduct file transfer operations and chromatographic control using the DEC Microvax II. Three RS-232 interfaces and analog-digital (A-D) converters were purchased to interface to the STDS and other laboratory equipment. Computer software to allow chromatographic data to be taken by the Microvax II was purchased. This computer software included routines which allowed methods, sequences, reports and reanalysis of raw data to be accomplished. In addition, the software was able to perform multi-level calibrations, baseline reconstruction and interactive graphics, directly from the VAX.

For this project, we had to purchase software that allowed the existing VAX computer to take chromatographic data directly from existing laboratory equipment. Because the software had to perform

data acquisition, post acquisition data analysis, and interactive graphics, a comprehensive software package was needed. It is not the sort of software package that could have been written by the University of Dayton, primarily because of its complexity. The source that we used was Nelson Analytical; the product they made for this kind of application is called "Access Chrom." In addition to installing the software and the A-D converters, PE Nelson Analytical provided demonstration and training for their products, and the necessary documentation in the form of product manuals.

Task: 12
Title: Multidimensional Gas Chromatography
Principal Investigator: Mr. Wayne A. Rubey
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: January 1990 - December 1991

Reports or Technical Information Generated:
Informal Technical Information and Viewgraphs

Task Description:

The Fuels Research Group (WL/POSF) at Wright Patterson AFB is interested in the ability to resolve, as completely as possible, all chromatographic solutes from one another in a complex hydrocarbon matrix such as jet fuel. To this end, this group has been investigating methods of increasing resolving power in a chromatographic system such as increasing column length by connecting multiple columns together. However, it is often desirable to increase resolving power by invoking a technique called multi-dimensional gas chromatography (MDGC). This technique is quite powerful in that it allows one to disengage solutes which may otherwise coelute by directing certain solutes to different chromatographic columns with different stationary phases.

With respect to aviation turbine fuels, MDGC techniques allow the user to acquire very descriptive analytical data in a relatively short period of time.

The Fuels Branch (WRDC/POSF) has at its disposal, a Hewlett Packard 5890B Mass Selective Detector 5890 A gas chromatograph with a 5970B Mass Selective Detector (MSD) and data storage capability. This collection of instrumentation was modified to conduct multi-dimensional gas chromatography (MDGC) using column arrangements suggested by UDRI. There were a number of physical modifications of the equipment which had to be made:

a) installation of tubing and valving arrangements
b) cryogenic trapping capability for switching valve
c) installation or pressure gauge different than that currently on GC system
d) removal of autosampler
e) installation of two capillary columns to be used in the MDGC analysis

Summary of Results:

Due to the fact that the GC-MS instrumentation was required for various other projects, this system for multi-dimensional gas chromatography could not be developed. Parts purchased to modify the

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26

Task: 13

Title: Determination of the Shelf-Life of Oil Calibration Standards for Portable Wear Metal Analyzer (PWMA-2)

Principal Investigator: Dr. Costy Saba

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start/Stop Dates: October 1989 - June 1992

Reports or Technical Information Generated:

Letter Status Reports

C. S. Saba, Determination of the Shelf-Life of Oil Calibration Standards for the Perkin-Elmer P.W.M.A., UDR-NM-MO-92-07, October 1992

Task Description:

At the time of task initiation, the Fuels Branch had recently acquired a Portable Wear Metal Analyzer, (PWMA-2) a graphite furnace spectrometer which requires three oil calibration standards blended in a synthetic non-mineral fluid and containing nine elements (low range), two elements (high range) and one element (Si). These standards were new in the Air Force inventory and did not have an assigned shelf-life.

The task required the University to determine the maximum usable shelf-life of the oil calibration standards required to standardize the PWMA-2 spectrometer used in the Air Force Oil Analysis Program.

This was accomplished by first developing a procedure and preparing the necessary primary reference standards (PRS) for the various concentration levels (0%, 30%, 50%, 100%) in both low range and high range levels. A special PRS was required for the element silicon (Si). These PRS were then analyzed using the PWMA spectrometer.

Summary of Results:

Because of time limitations, the shelf life testing was conducted on only Mobil (MCP1201) for a 9-month period. The 9-month old Mobil (MCP1201) concentrations were compared to the fresh standard in the same oil. The results of the differences, mean and standard deviation on five data points for each of the nine metals were presented to the sponsor.

The calibration standards in Mobil (MCP1201) exhibited good stability over 9-month period of evaluation. Only high range iron showed large deviation while minor deviations were observed for all the other elements.

Task: 14
Title: Laboratory Software Installation and Training
Principal Investigator: Mr. Nathan Vonada
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: August 1989 - December 1989

Reports or Technical Information Generated: None generated.

Task Description:

In this task, a senior computer science undergraduate was assigned to act as Microvax system manager. Under this task, the system manager was responsible for maintenance of the VAX mainframe and terminals, scheduling usage time, assigning and monitoring accounts and installing new software.

Summary of Results:

Mr. Vonada acted as system manager during this period. He installed and supported the "Access Chrom" software, "Connect" software and other chromatographic and data management software. All of the software used and the programs and procedures written by Mr. Vonada were placed in the VAX for interactive usage. He spent a good deal of time training government employees and on-site contractors about procedures on the Microvax.

Task: 15
Title: Gold-Lined Test Cell Assembly and Heated Transfer Line
Principal Investigator: Mr. Richard C. Striebich
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: 15 September 1989 - 15 September 1990

Reports or Technical Information Generated:
None Generated

Task Description:

This task involved two separate sub-tasks. First, production of gold-lined test cells using the gas-phase tubular reactor (TCA-IV) with a layer of gold deposited on the inner surface. The use of this test cell assembly allowed an experiment to be conducted to investigate the catalytic or surface effects of the gold and quartz. The data with the gold-lined test cell could be compared to the data with the quartz tubular test cell. Second, the heated transfer line project was initiated but the availability of the instrument became so limited that the transfer line could not be installed. The FTIR that was to be used for this program was constantly running liquid phase samples. By connecting the light pipe to the gas chromatograph, the instrument could not be used in its original configuration. Therefore, the decision was made to leave the liquid phase FTIR as it was.

Summary of Results:

Neither of these tasks were successfully completed.

In the case of the gold-lined test cell, all attempts to gold line the tubular flow reactor were unsuccessful. The length of the quartz tubing would not allow for an even distribution of gold lining along the flow path. Therefore, we decided to gold-line shorter lengths of tubing which could be used as inserts in the catalytic reactor delivered under Task 3. The quartz flow reactors already constructed were used in the gas phase STDS. The heated transfer line components were purchased but never installed. They were finally used in other Air Force projects due to the change in instrument availability as described above.

Task: 16
Title: XPS Analysis of Stained Boron Nitride Specimen
Principal Investigator: Mr. James Hoenigman
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: 15 September 1989 - 30 September 1989

Reports or Technical Information Generated:
Letter report to Dr. Fritts WL/POOX

Task Description:

High Resolution XPS analysis was desired for three regions of interest before and after ion etching.

Summary of Results:

XPS analysis was successfully completed and a final letter report was provided to the sponsor explaining the results.

Task: 17
Title: Low Pressure Catalytic Test Cell Upgrade
Principal Investigator: Mr. Richard C. Striebich
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: January 1990 - May 1990

Reports or Technical Information Generated:
Low Pressure Catalytic Test Cell Assembly: Installation and Operation Manual UDR-DR-91-99

Task Description:

In a prior task (Task 03), UDRI designed and constructed a low pressure vapor phase catalytic test cell for the System for Thermal Diagnostic Studies (STDS). This cell was subsequently installed in our STDS and performed very well in its current configuration. Under this task, additional work was necessary to make final adjustments to the cell design and operation, and to carry out initial "proof of concept" reactions. The final step in this task was to deliver the test cell to the Air Force, install it and train government personnel in its operation. A schematic of the final test apparatus is provided as Figure 6.

Summary of Results:

This task required the purchase of various pieces of hardware, samples of reactant, and standardization chemicals to complete the final microreactor test cell design. The reaction cell and the necessary connections to the STDS mainframe permitted operation to 1000°C and the residence times at temperature of from 0.1 to 10 seconds.

The test cell assembly was installed on the STDS in Room 206, Bldg. 490. Training was conducted by the principal investigator to allow Jim McCoy to conduct a series of experiments concerning olefin methathesis under catalytic conditions. The design of the cell was such that the catalyst could be treated in-situ using available heating systems and redirecting gas flow to the reactor.

The experiments conducted as a result of this project were summarized in at least two technical papers, including a doctoral thesis.

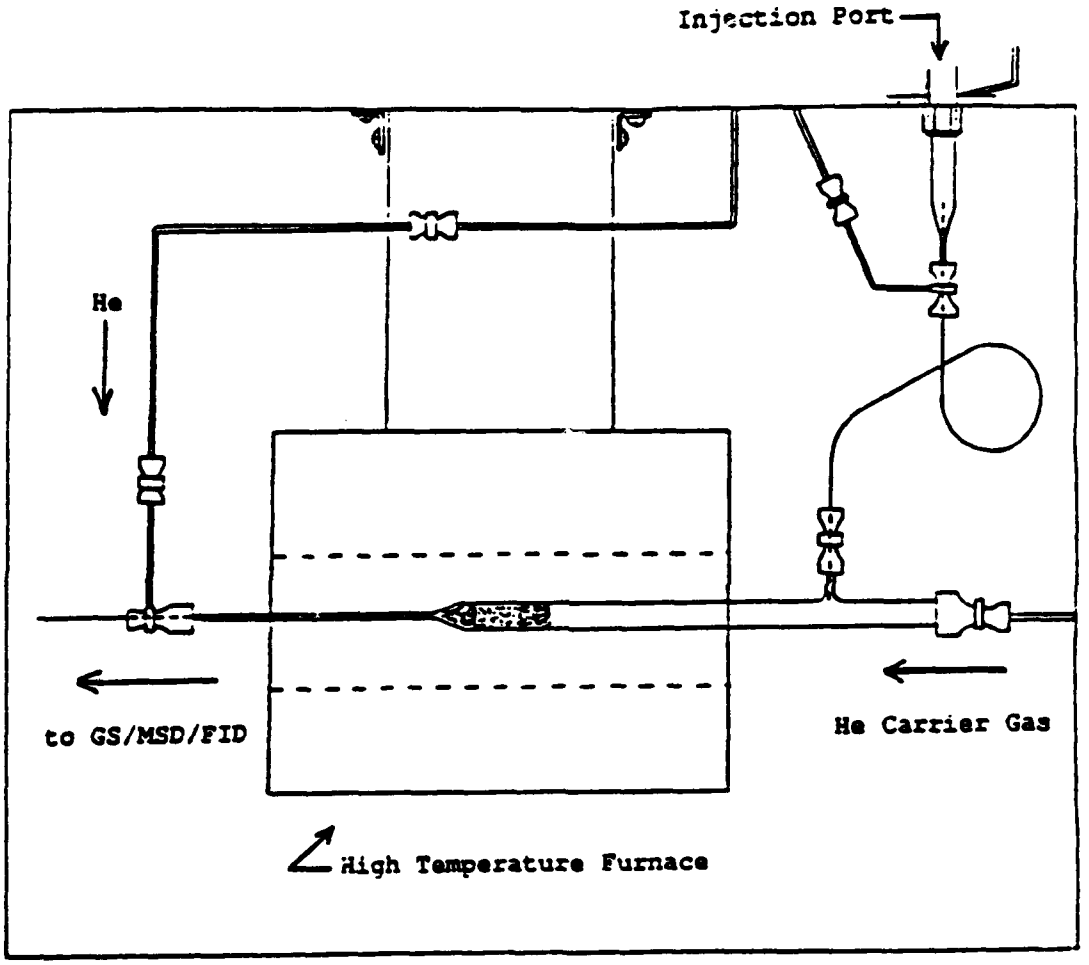


Figure 6. Catalytic Reactor Chamber.

Task: 18
Title: Preparation of Single Crystals of p-Hydrogen
Principal Investigator: Dr. Takeshi Oka
Affiliation: University of Chicago, Chicago, Illinois
Start/Stop Dates: 15 February 1990 - 15 October 1990

Reports or Technical Information Generated:
University of Chicago Technical Report, 2 papers to learned journals

Task Description:

The object of this project was to purchase and construct various cryogenic parts and assemble them into an apparatus which would enable the preparation of solid hydrogen single crystals with exceptionally high purity.

Summary of Results:

The following results were achieved in the area of crystal making. The concentration of the ortho-hydrogen was reduced from 0.2% down to 0.06% by pumping harder on the liquid hydrogen which was used to cool the ferric oxide catalyst for the ortho-para conversion.

A cryogenic dewar was acquired and assembled which, together with the new temperature controller, allowed optimization of temperatures as crystals grew. A new method of growing crystals was successfully developed by introducing into the sample cell a continuous flow of high-purity para-converted hydrogen gas rather than the pulsed gas as had been done so far. This allowed better control and monitoring of the process of crystal growing.

Task: 19
Title: Electric Field Measurement in Flames
Principal Investigator: Dr. Roger Becker
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: March 1990 - October 1990

Reports or Technical Information Generated:
R. J. Becker, Electric Field Measurement in Flames, Final Report, October 1990

Task Description:

The primary goals of the program were to design a vacuum chamber for low pressure spectroscopy in flames, to order the necessary components, and to construct and assemble the hardware. Another major objective was to make an available analysis program operational. These tasks were considered to be the most critical factors in implementing the Rydberg technique. During the course of this work a third objective materialized; the demonstration of the method in an atmospheric pressure flame.

Summary of Results:

A system for measuring the Stark-induced line shifts in the Rydberg spectra of single atoms in low pressure flames was installed. This system was designed to develop a non-intrusive method for studying electric fields in flames. The technique was tested at atmospheric pressure on a second modified system using a small flat-flame burner. The experimental results obtained on the atmospheric system are highly encouraging and give some credence to the possibility that the Rydberg method can be used in laboratory burners to provide useful data applicable to practical combustors.

Task: 20
Title: RJ-7 High Density Fuel Development
Principal Investigator: Dr. Lew Hall
Affiliation: Sun Refining and Marketing Co., P. O. Box 1135, Marcus Hook, PA 19061
Start/Stop Dates: 1 April 1990 - 1 October 1990

Reports or Technical Information Generated:
RJ-7 High Density Fuel Development, Final Report

Task Description:

Previous work demonstrated the feasibility of producing RJ-7 missile fuel. WL/POSF was then issued a draft military specification for RJ-7 missile fuel. The sub-contractor was required to explore the various processes and technologies involved in producing RJ-7 and determine a process scheme resulting in a fuel that meets the requirements of the draft specification at the lowest possible price. The sub-contractor was required to verify the process technology and to produce a 4-gallon sample for delivery to WRDC/POSF at the conclusion of the task.

Summary of Results:

A new formulation as RJ-7 consisting of a ternary blend of perhydrogenated cyclopentadiene trimer (CPD Trimer), the dihydro derivative of the adduct of cyclopentadiene and indene (CPD/Indene) and JP-10 was developed. This formulation closely approximates the target of a minimum heating value of 150,000 Btu/gal but is significantly higher in viscosity at -65°F. The freezing point of the fuel is approximately -100°C.

Sufficient components were produced to formulate approximately seven gallons of RJ-7 fuel of the following composition:

Table 1. Composition of RJ-7 Fuel

Component	Wt.%	Vol.%
CPD Trimer	54.0	53.1
Dihydro CPD/Indene	24.0	23.1
JP-10	22.0	23.8
BHT (Antioxidant)	100 ppm	---
Icing Inhibitor	---	0.12

Properties of the resulting fuel blend are listed in the following table:

Table 2

RJ-7 Fuel Properties

(Sample No. 882872)

Property	Value	ASTM Method
Saybolt Color	+29	D156
Flash Point, °F	172 (176)*	D93
Specific Gravity	1.0153 (1.0154)*	D1298
Density, g/cm^3	1.0116 (1.0117)*	
Viscosity, cSt -40°F -65°F	 373 (374)* 2102 (2259)*	D445
Existent Gum mg/100 mL	34 (39)*	D381
Heat of Combustion Net Btu/gal Net Btu/lb	 150, 905 (151,139)* 17,893 (17,919)*	D240
Carbon, %	89.4	
Hydrogen, %	10.5	
Freezing Point, °F	>-110	DTA

*Duplicate Determination

The bulk of the fuel sample (approximately 6.5 gallons) was shipped to the Naval Weapons Center, China Lake, CA to the attention of G. W. Burdette and a small sample (1 pint) sent to the Fuels and Lubricants Directorate (POSF) at Wright Patterson AFB to the attention of Dr. J. R. McCoy.

In addition, a 1-pint sample (No. 882871), in which the dihydro CPD/Indene component of the RJ-7 formulation was replaced with the perhydrogenated derivative, was prepared and sent to China Lake.

Task: 21
Title: Thermal Stability Simulation Assessment
Principal Investigator: Kenneth E. Binns
Affiliation: Consultant to University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: 15 March 1990 - 30 December 1990

Reports or Technical Information Generated:
Two Technical Memoranda

Task Description:

The objective was to assess the requirements for accurate simulation of the performance of advanced jet fuels and additives in aircraft components. To this end, the University obtained the services of a highly specialized consultant to: 1) assess aircraft fuel/fuel system simulation requirements necessary to demonstrate the potential of advanced fuels and additives, and 2) prepare an assessment of the requirements needed to qualify advanced thermally stable fuels for use in Air Force aircraft.

Summary of Results:

The consultant performed on-site reviews of the Air Force Reduced Scale Fuel System Simulator (RSFSS) and made specific recommendations, especially per the range of fuel temperatures at which to operate the simulator. At a later date, he reviewed the simulator tests of pipeline drag reducer (PDR) additive and again made specific recommendations germane to future test procedures to be employed in such testing.

Task: 22
Title: Application of Coherent Anti-Stokes Raman Spectroscopy
Principal Investigator: Dr. Perry Yaney
Affiliation: University of Dayton Physics Department, Dayton, Ohio, 45469
Start/Stop Dates: 12 March 1990 - 30 September 1990

Reports or Technical Information Generated:
Presentation of AIAA Minisymposium, March 29, 1990, Dayton, Ohio
Related Document: Carillo, et al., Development of a High Resolution Coherent Anti-Stokes Raman Spectroscopy System for Use in the Study of Electrical Discharges in Nitrogen, July 1990.

Task Description:

This task was initiated to continue research being conducted in on-base facilities at Bldg. 450, Area B, Wright Patterson AFB, Ohio. A new laboratory was prepared to accept a system to conduct Coherent Anti-Stokes Raman Spectroscopy (CARS), and data acquisition systems, including A/D converters, were also set up and debugged.

The research associated with the CARS system was mainly to develop spatial axial and radial temperature profiles. In addition, the research was to focus on the characterization of the behavior of the individual rotational transitions in local regions of the nitrogen discharge. Computer codes were both developed and modified to collect and interpret high resolution spectra.

Summary and Results:

Extensive CARS measurements were carried out. These series of runs each required week-long preparations followed by long, uninterrupted data recording sessions. We analyzed the raw data using a series of complex, time-consuming computer-fitting procedures. The studies uncovered instabilities in the discharge device which greatly complicated the analyses. The final result of this work was a somewhat better understanding of the nature of the discharge and modifications of the data-recording procedures.

The results of these studies were presented by Mr. Carillo at the AIAA Minisymposium, March 29, 1990, Dayton, Ohio, and at the spring meeting of the Ohio Section of the American Physical Society, April 27-28, 1990, Denison University. Mr. Carillo completed his Masters thesis entitled, "Development of a High-Resolution Coherent Anti-Stokes Raman Spectroscopy System for Use in the Study of Electrical Discharges in N_2," in July 1990.

The design and outfitting of the new laboratory located in Room D120 of Building 450 was completed up to the actual moving of the CARS system to the new lab. This delay was necessary to provide adequate time to design and develop a new discharge chamber. Furthermore, additional measurements were needed making it inappropriate to proceed with the final stages of the move. The design of the complete CARS and optical spectroscopy system is complete in virtually every detail.

All of the parts needed to construct the new data acquisition interface were selected and purchased. The design and layout of the module which housed the interface electronics and cable connectors were completed. The main obstacle to bringing the new data acquisition system up to operational status was the development of the software. A new software package is now available for which familiarity is needed before the required programs can be developed.

Task: 23

Title: Support and Modifications for the Lubrications System for Thermal Diagnostic Studies (STDS)

Principle Investigator: Mr. Wayne A. Rubey and Mr. Richard C. Striebich

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start/Stop Dates: June 1990 - December 1990

Reports or Technical Information Generated:

W. A. Rubey and R. C. Striebich, Supplemental Manual for the System for Thermal Diagnostic Studies (STDS)

Task Description:

The System for Thermal Diagnostic Studies (STDS) was placed in the Lubrications Lab (Bldg. 490) in late 1989. Since that initial instrumentation set-up, hundreds of runs had been conducted in pyrolytic mode, investigating the high-temperature thermal-degradation characteristics of thermally stable lubricants (polyphenylethers). However, the oxidative stability of the polyphenylether lubricants was of significant interest, and modifications of both the lubrications laboratory and the STDS instrumentation had to be made to address this new research area. In addition, new operating procedures needed to be developed to address oxidative studies with solvent bearing samples.

A quartz test cell assembly to conduct basic thermal decomposition experiments was inadvertently broken during pyrolytic testing. This test cell needed to be repaired and a new test cell reinstalled into the system.

Summary and Results:

Many repairs and modifications of the system were performed under this task. The broken test cell and quartz inserts for the injector were repaired and spares for each of these pieces were delivered for the system. A new procedure was developed for removal of sample solvent when conducting a thermal decomposition experiment. This involved injecting the sample, dissolved in a solvent, onto quartz wool and gently heating the thermal reaction compartment of the STDS to vaporize the solvent rather than the less volatile solute of interest (in this case, polyphenylether). After transporting the vaporized solvent out of the system, the thermal reaction compartment could then be heated to temperatures high enough to completely volatilize the polyphenylether material (up to 300°C).

Additional technical information, in the form of a supplemental manual for the STDS, was delivered under this task. It included a number of procedures for conducting specific experiments, as well

as procedures for installing and removing individual components of the STDS, such as the test cell assembly and the quartz inserts.

Task: 25
Title: Measurement of Dissolved Oxygen in Jet Fuel
Principal Investigator: Mr. Wayne A. Rubey
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: June 1990 - December 1990

Reports or Technical Information Generated:

Task Description:

This program was conducted by designing and building an analytical system to measure the levels of dissolved oxygen in jet fuel to less than 1 part per million (ppm). In addition, this instrumentation system was directly interfaced to the Phoenix rig, a thermal stressing device which was then under development at Wright Patterson AFB. The Phoenix rig incorporated three separate streams of fuel flow, i.e., two before and one after exposure to high temperatures. Each of these fuel lines could be sampled with the analytical system which was developed.

This task had two major objectives. The first was to design and assemble a system for conducting analysis of entrained gases, primarily oxygen. A second objective of this project was to interface the oxygen detection method to the Phoenix rig using gas sampling valves and, if necessary, heated transfer lines.

A dedicated in-line gas chromatographic system, which utilized a three-member tandem separation column arrangement, was developed. With the use of this closed and continuous GC system, analyte separation, detection, and fuel backflush were accomplished rapidly, and detection capabilities for the various analytes were found to be less than 50 parts per billion. Thermally-stressed, high pressure, continuous flowing fuel streams were sampled every 15 minutes, thereby allowing frequent monitoring of important changes in the dissolved gas portion of the fuel. A technical report describing the operation, maintenance and troubleshooting for this system was developed and delivered to the Air Force. A diagram of the system is provided in Figure 7. The system was installed in conjunction with the Phoenix Rig, allowing the fuel oxygen concentration to be measured after thermal stressing. To date, this system has operated very successfully with consistent and precise values for dissolved oxygen being obtained.

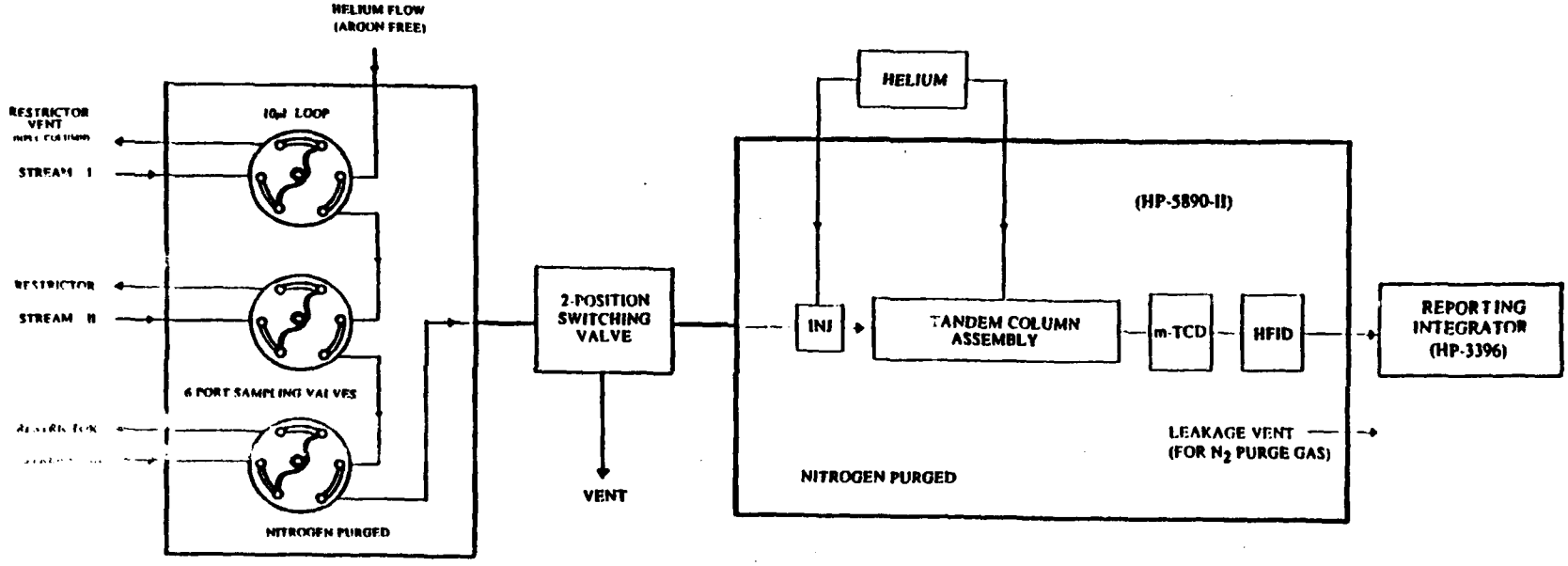


Figure 7. Abbreviated Schematic for the Dissolved Oxygen Analytical System.

Task: 26

Title: Thermal Oxidative Stress Test for Elucidating Fuel Chemistry and Determining Additive Efficiencies

Principal Investigator: Dr. William Schulz

Affiliation: Eastern Kentucky University, Department of Chemistry

Start/Stop Dates: July 1990 - July 1991

Reports or Technical Information Generated:

W. Schulz, et al., Development of a Thermal Oxidative Stress Test for Elucidating Fuel Chemistry and Determining Additive Efficiencies, Final Report, July 1991;

W. Schulz, et al. WL-TR-93-2015, Analysis of Deposit Precursors in Jet Fuels Using Fourier Transform Infrared Spectroscopy, Final Report, Contract F33615-87-C-2714, January 1993.

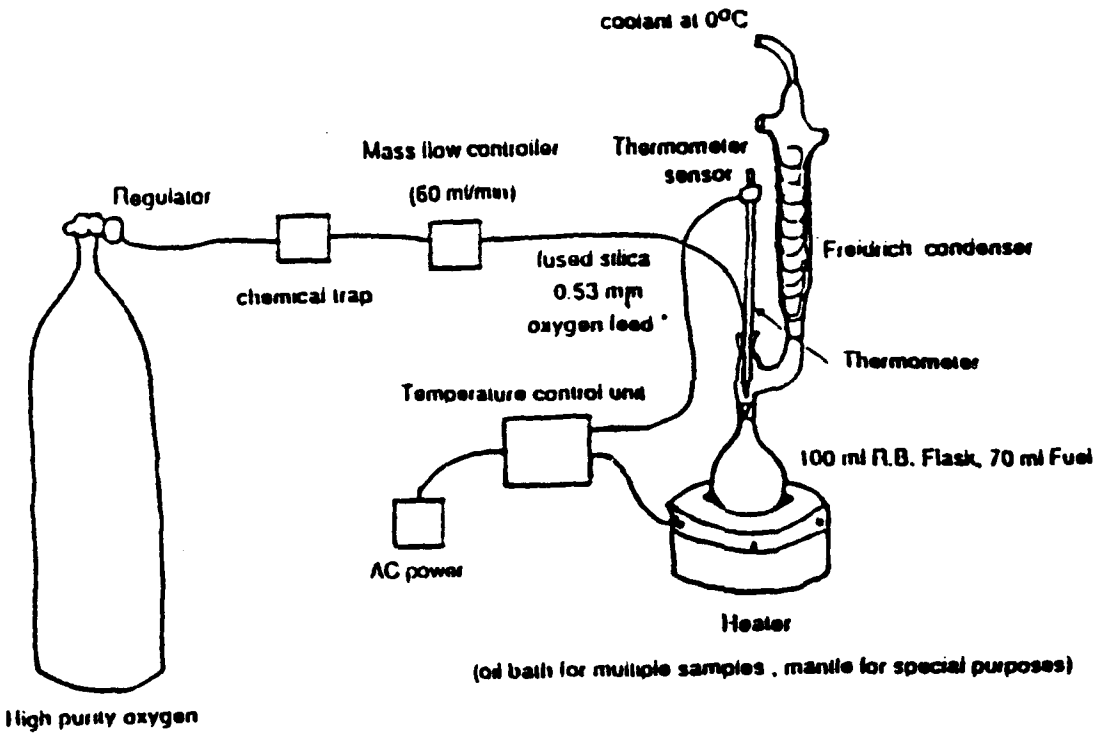
Task Description:

The purpose of this task was to develop an experimental arrangement to investigate the oxidation of jet fuel in an ambient pressure flask. These types of experiments were important in the area of jet fuel thermal stability because they allow the investigation of how the fuel is changing in addition to allowing one to extract the solid materials forming in order to determine the nature of the deposits. The oxidative stress test was developed as a means of screening and comparing additives for their effectiveness in preventing oxidation, as measured by the amount of deposits (soluble gums, insoluble gums and insoluble solids) formed in the flask upon heating.

Summary and Results:

Significant progress was made in developing a thermal oxidative stress test under this task. The results of this task were summarized in the final report for this project entitled, "Development of a Thermal Oxidative Stress Test for Elucidating Fuel Chemistry and Determining Additive Efficiencies," July 1991. In addition, a technical report was generated from a master's thesis resulting from the work performed on this project.

The experimental apparatus has already been used for a wide variety of experiments on the thermal stability of jet fuel. The main parts of the apparatus are depicted in Figure 8. Further experimental details are described in the related reports.



*Deactivated fused silica oxygen fed reaches bottom of fuel in R.B. flask

Figure 8. Schematic Diagram of Modified Flask Test for Thermal Oxidation of Fuels

Task: 27
Title: Magnetic Property Measurements for Superconductors
Principal Investigator: Dr. Binod Kumar
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: 30 April 1990 - 30 July 1990

Reports or Technical Information Generated:
Technical Memorandum and Informal Technical Information
Invention Disclosure: Fast Ion Conductors

Task Description:

The magnetic properties of high temperature superconductors need to be assessed for space platforms which may contain high power sources and pulsed power devices, some of which may contain magnetic bearings. High-temperature superconductors can provide lightweight high-magnetic energy density solutions to these problems. In order to accomplish a significant weight savings in spacecraft power devices, it is necessary to fabricate samples of high-temperature superconductors and quantify the magnetic properties in appropriate sample holders at various operating temperatures.

This task was initiated to conduct the following: fabricate and appropriately mount high-temperature superconductor samples to allow properties to be measured in any or all of the following: a) AC susceptometer, b) DC SQUID susceptometer, c) vibrating sample magnetometer, d) variable temperature, variable magnetic field, DC transport current apparatus, e) inductive AC transport current apparatus, and f) scanning electron microscope; and conduct magnetic property and physical morphology measurements on any or all of the above pieces of experimental apparatus to determine the optimized critical current density of the samples which were prepared.

Summary and Results:

The work conducted under this program resulted in an invention disclosure for "Fast Ion Conductors." Fast ion polymers have application in the area of solid state batteries and sensors. A mechanical device was proposed to enhance the ionic conductivity of solid polymers. These and other results are reported in the technical memorandum which was submitted previously for this task.

Task: 28
Title: An Experimental Study of Hybrid Nozzles
Principal Investigator: Dr. Richard S. Tankin
Affiliation: Northwestern University, Department of Mechanical and Nuclear Engineering
Start/Stop Dates: June 1991 - September 1992

Reports or Technical Information Generated:
R. Tankin, Final Report on An Experimental Study of Hybrid Nozzles, September 1992

Task Description:

The process by which fuel is atomized and injected into the combustor of a gas turbine engine is highly complex and sensitive to the fluid conditions within the nozzle as well as gas conditions at the nozzle discharge plane. Modeling the details of the liquid breakup process may be beyond the scope of our current capabilities. An alternative approach, based on information entropy principles, has been evolving and offers the potential of accurately predicting the distribution of droplet size and velocities immediately after the liquid sheet has disintegrated. It is a global approach that is sensitive to conditions within the nozzle that affect the liquid sheet formation. These conditions are being rapidly and significantly changed as fuel systems play an increasing role in the thermal management strategy of modern aircraft. We anticipate that the fuel entering the nozzle will be superheated, thermally stressed, and multi-phase at various flight conditions. The influence of the fuel state on atomization and distribution within the combustor is not known and may be impossible to predict with conventional modeling approaches. The maximum entropy approach is a promising alternative for predicting these influences.

The purpose of this program was to modify the existing maximum entropy code, which predicts liquid sheet breakup from an axisymmetric pressure atomizing fuel nozzle, to predict the breakup process in air assist and hybrid nozzle configurations. The resulting code was designed to permit significant variation in the fluid thermodynamic state (liquid, gas, supercritical fluid, and bi-phase flow) and in the interfacial momentum exchange between nozzle air and fuel. Flexibility in the latter parameter should permit the energy of atomization to be between 5 and 100% in the fuel with the balance of energy in the air stream. The extremes of this variation represent an air assist nozzle (5% energy in fuel) to a fully pressure atomizing nozzle (100% energy in fuel).

Results and Summary:

A hybrid nozzle is a pressure atomizer that uses air to assist in the atomization of the spray and the patternation. The Allison nozzle was used during the summer of 1991 to determine if a bimodal size

distribution could be observed is a hybrid nozzle. When operated at low flow rates, the drops that form just downstream of the breakup region exhibited a bimodal distribution. In the experiments conducted during the period under consideration, the effects of the air flow on the size and velocity distributions of the drops were examined.

Measurements were made just downstream of the liquid sheet breakup region. Using a combination of photographs and droplet distribution measurements, the hybrid spray nozzles were characterized.

Concurrent with these experimental studies, a numerical program was developed at Northwestern University that could model the air flow for this rather co[illegible]ed geometry. Research of this kind is continuing under other programs.

Task: 29
Title: Alkali Plasma Diagnostics
Principal Investigator: S. Douglas Marcum
Affiliation: Miami University, Oxford, Physics Department, Oxford, Ohio
Start/Stop Dates: September 1991 - September 1992

Reports or Technical Information Generated:
S. D. Marcum, Alkali Plasma Diagnostics, Final Report, September 1992

Task Description:

The purpose of this task was: 1) conduct emission spectroscopic measurement in a variable temperature hot-cathode argon-cesium discharge. The cathode temperature and discharge current density dependent emission intensity data should be compared with the calculated intensities obtained from a detail balance rate equation approach; 2) perform absolute intensity measurements by using a black-body radiation calibration procedure to permit electron density and electron excitation temperature measurement.

This task was intended primarily to more carefully quantify the electron density in the tail of the (non-Maxwellian) electron energy distribution function found in such plasmas and, secondarily, to extend the previous measurements over a wider range of discharge current densities and cathode temperatures. At the low current densities used thus far, the bulk electron density is of the order of 10^9 cm^{-3}. Under such conditions, it is possible to construct a simple model that allows calculation of absolute cesium excited state densities. The resulting absolute emission intensities are then easily computed and can be compared to spectroscopic measurements to yield electron excitation temperature.

This work required the modification of the discharge cell and its heating system to allow for the experimental procedures required for absolute intensity calibration of the spectroscopic system. At the higher cathode temperatures used (>1000 K), sufficient visible near IR emission from the hot cathode allowed use of the glowing cathode as a "built-in" blackbody calibration source. However, owing to the need for extreme precision in absolute calibration of spectroscopic systems, an NIST-traceable standard lamp was purchased and used as a check on the hot-cathode-based calibration. Those complementary absolute intensity calibrations provided the confidence level needed to extract accurate electron densities from the studied plasmas. Additionally, the standard lamp provided a means of easily checking the calibration from time-to-time without reconfiguring the optics to view the hot cathode. This is desirable in alkali metal plasma systems since deposits of thin films of cesium on the viewports can occur that affect their transmission characteristics.

Summary of Results:

Electron excitation temperatures have been measured in a low pressure (0.05 Torr Cs, 2 Torr total pressure) argon-cesium discharge that uses a heated cathode (900-1100 K). The excitation temperature determinations are based upon a model that allows calculation of cesium excited state densities for low electron density ($<10^{11}$ cm^{-3}). The model assumes that the dominant creation processes for excited states are electron impact excitation from the ground state and radiative cascade from higher levels, while destruction is by spontaneous emission. Maxwellian electron energy distributions were used and the plasmas were considered to be optically thin. The model indicates that cascade contributions to the production of excited states can be as high as 50% for some cesium levels. Predicted emission spectra with cascade contributions to spontaneous emission intensities agree well with measured spectra except for radiation trapped transitions from low nP states to the ground state. Excitation temperatures are determined by fitting measured and calculated spectra.

Task: 30

Title: Klystron Simulation Model

Principal Investigator: Dr. Bruce Goplen and Dr. K. Nguyen

Affiliation: Mission Research Corporation, 8560 Cinderbed Road, Suite 700, Newington, VA 22122

Start/Stop Dates: July 1990 - September 1990

Reports or Technical Information Generated:

B. Goplen, et al., Klystron Simulation Model, Interim Report MRC/WDC-R-272, September 1990

Task Description:

The purpose of this task was to develop and validate a detailed simulation model of a klystron. This model was based on blueprints and/or technical specifications of the klystron. The features of the model to be developed were as follows:

1. A two-dimensional model was developed for the electron gun, all klystron cavities, and the collector. This model was to closely adhere to the actual physical dimensions of the klystron. Cavity-resonant frequency measurements were made for a direct comparison with experimental data.

2. The incident power pulse to the electron gun was represented using a voltage algorithm. The electron beam was represented using macroparticles created at the cathode surface using a field-emission algorithm. The gun model was validated by measuring gun current and comparing with experimental data.

3. The external RF source for the buncher cavity was also represented using the voltage algorithm.

4. Extraction of RF from the remaining cavities was represented using a combination of a time-biased field algorithm and a conductivity algorithm.

To validate this model, the investigators measured power extracted from each cavity and compared to experiment results. Conventional efficiency and gain measurements were also made. After the model was validated, the resulting spent-beam properties were used to measure energy deposition as a function of position along the collector surface. Both CW and time-dependent measurements were made.

Summary of Results:

The Klystron simulation model was developed as identified in the task description above. The model is described in great detail in an interim report MRC/WDC-R-272, "Energy Deposition in a VKP7555S Collector." It was implemented in cylindrical coordinates in MAGIC. The final simulation consisted of 17,040 electromagnetic cells and created 92,750 particles over 18,550 time steps (50 RF cycles). The simulation required about 14 hours to run on a VACCELLERATOR. Final results for electron trajectories, axial phase space and collector energy deposition were reported. The measured energy in the output cavity at the conclusion of the simulation was 4.4 x 10(-4) joules, which would correspond to an efficiency of 35%. The total heating rate in the collector was 77 kW.

Task: 31 and 31A
Title: Lithium Rechargeable Battery Investigation
Principal Investigator: Dr. Binod Kumar
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: July 1990 to October 1990

Reports or Technical Information Generated:
Letter report; informal technical information
B. Kumar, Polymeric Materials for Battery Applications, UDR-TR-90-96, WRDC-TR-90, October 1990

Task Description:

The objective of this task was to:

1. Investigate the revisibility and chemical stability of lithium anodes in nonaqueous liquid electrolytes of the type used in $LiSO_2$, Li-CoO_2 and Li-$CuCl_2$ systems. These electrolytes were: $LiAlCl \bullet 6SO_2$, $CO_2 + LiAsF_6$+$LiBF_4$/MF and $LiAsF_6$/PC+EC. Also, additives were investigated for improving lithium anode efficiency and reversibility.

2. Characterize solid electrolytes (lithium conducting glasses, ceramics and polymers) with respect to their mechanical/chemical compatibility with lithium and their conductivity as a function of temperature/doping concentration.

Summary and Results:

Electrochemical studies of select solvent/solute systems were conducted to determine the effect(s) which solvent and/or electrolyte modifications have upon stability and electrochemical reversibility of lithium anodes. Of particular interest was the effect(s) which electrolyte modifications might have upon the width of the electrolyte voltage window, energy/columbic efficiency, electrochemical reversability, magnitude of the exchange current density and chemical stability of the system. Also, solid electrolytes (lithium conducting glasses, ceramics and/or polymers) were fabricated and characterized for conductivity, chemical/mechanical compatibility, mechanical/electrochemical properties as a function of temperature and practicality as an electrolyte for lithium rechargeable batteries.

Task: 32

Title: Data Acquisition System for Determining Particle Size Distribution in Lubricating Fluids

Principal Investigator: Dr. Costy Saba

Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132

Start/Stop Dates: August 1990 - June 1992

Reports or Technical Information Generated:

R. Kauffman, et al., Data Acquisition System, UDR-TR-92-130, December 1992

Task Description:

The purpose of this project was to investigate the potential of a Data Acquisition System to reduce the number of undetected engine failures by the Air Force. Failures of Air Force OAP in predicting emminent engine failure can be related, in some cases, to the particle size detection limits of the A/E35U-3(-3A). This data acquisition system, if proven successful, will enable the Air Force OAP to identify and replace the abnormal wearing component(s) prior to engine failure.

In order to improve the capability of the current spectometric oil analysis techniques to detect abnormal wearing component(s) prior to engine failure, the University of Dayton Research Institute (UDRI) developed a Data Acquisiton System which enabled the A/E35U-3(-3A) to determine particle size distribution and particle size composition, as well as the concentration of the wear debris in used lubricating fluids. Also, this data acquisition system was to be used with different types of fluid analysis spectrometers.

Summary and Results:

The data acquisition system for determining particle size distribution was designed, constructed and tested at UDRI laboratories in the first part of this project. Since particle size of various metals may be an early indication of engine wear and eventually engine failure, the Air Force was interested in locating these instruments at various active Air Force bases in order to predict engine failure by monitoring lubrication fluids.

One such system was constructed and was placed at the 3246 Field Maintenance Squadron (FMS) at Eglin Air Force Base, Florida. Personnel at the base were trained in the operation of the instrument and oil samples were monitored over a period of several months. Similarly, the 57EMS at Nellis Air Force Base and the 188th TFG/MA at Fort Smith, Arkansas, were provided with the data acquisition and

trained in its operation. Another data acquisition system at UDRI laboratories was used to monitor oil samples from the TAW, Milwaukee, Wisconsin.

To date, only submicron particles have been observed in these samples. The particle size must be more significant than submicron size for an indicator of engine failure. It should be noted that no engine failure occurred at the bases during the period tested. The conclusion is that predictions could be made using this instrument, but since no engines have failed, no predictions were made.

Task: 33
Title: Thermal Stability Simulation Assessment
Principal Investigator: Mr. Edward Binns
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start Stop Dates: December 1990 to September 1991

Reports or Technical Information Generated:
Technical Memoranda and Informal Technical Information

Task Description:

The Air Force has a fuel system simulator and wanted to assess the requirements for the accurate simulation of components using advanced thermally stable aircraft fuels and additives. This activity was carried out by interviewing and visiting key individuals in the government and industry. Effects of thermal instability on various aircraft engine components were documented for actual systems.

In performing this function, the principal investigator was to determine which experiments to perform on the Reduced Scale Fuel System Simulator in order to investigate the problems that were occurring in the actual systems in the field. Finally, the principal investigator was to suggest and document recommendations for improving the simulator system.

Summary of Results:

Mr. Binns was involved with collecting information on actual field thermal stability problems at Oklahoma City Air Logistics Center, San Antonio Air Logistics Center and other bases. Several areas of potential research were identified in augmentor spray bars and nozzles. This work initiated several research programs in the area of characterizing augmentor fouling patterns.

Mr. Binns was also involved in configuring the Fuel System Simulator to address specific aircraft testing. Figure 9 shows one such configuration that was obtained.

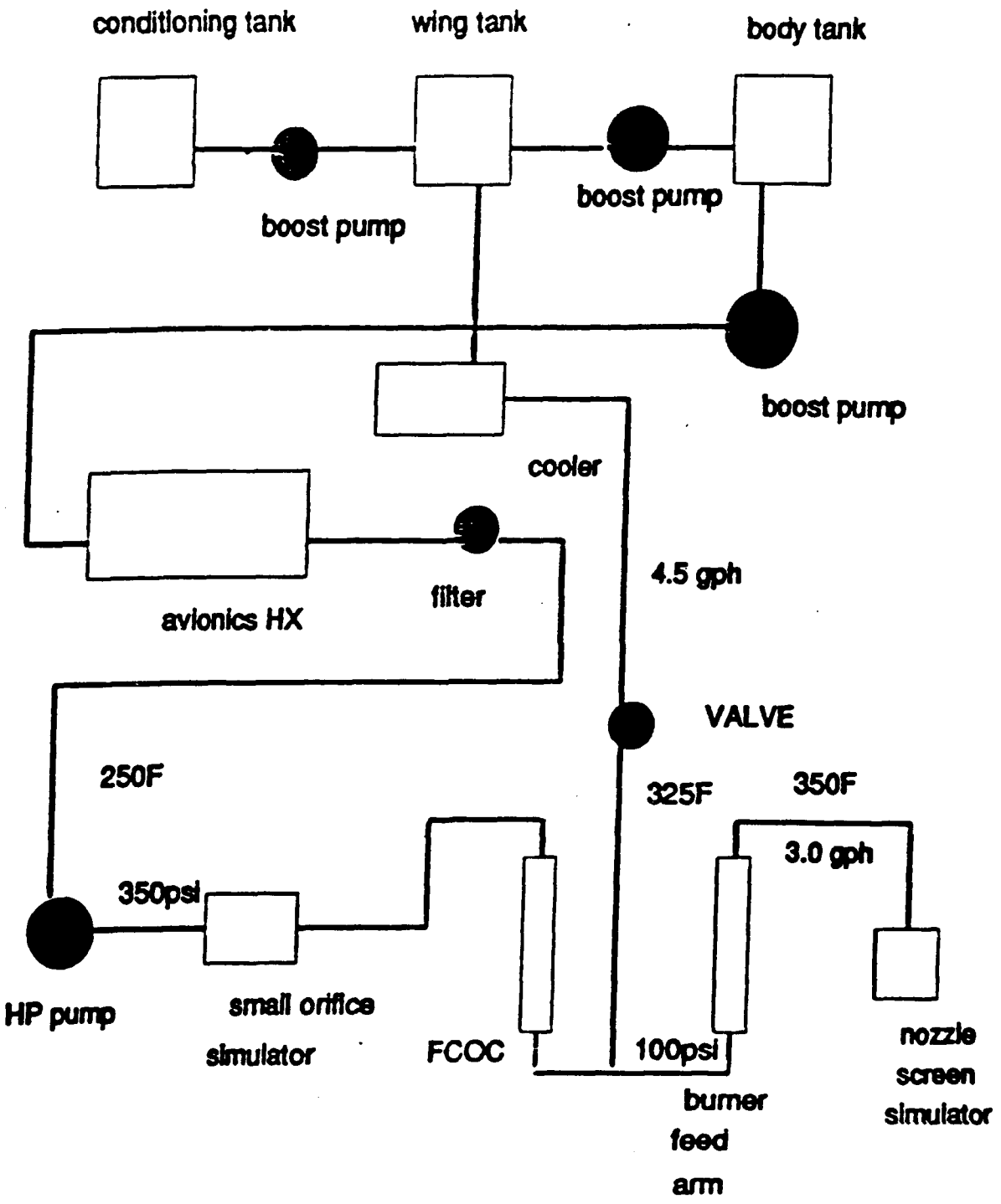


Figure 9. Advanced Fuel System Configuration Descent Condition.

Task: 34
Title: Evaluation of Jet Fuel Antioxidants Using the Remaining Useful Life Lubricity Evaluation Rig (RULER)
Principal Investigator: Mr. Bob Kauffman
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start Stop Dates: February 1991 to January 1992

Reports or Technical Information Generated:
R. Kauffman, D. A. Tirey, New techniques to predict and Evaluate the Effectiveness of Antioxidants in Jet Fuel, presented at the ACS, San Francisco, April 1992.
R. Kauffman, Antioxidant Effectiveness of Jet Fuel Additives Using RULER, UDR-TR-92-148, December 1992

Task Description:

The stability of aviation fuel is a major consideration in the design of aircraft fuel systems. During both storage and exposure to elevated temperatures, aviation fuels can form peroxides which decompose to yield soluble gums and eventually insoluble materials that can deposit on heat transfer surfaces, obstruct valves and filters in the fuel lines and degrade the performance of injection nozzles. Special chemical compounds are added to jet fuel to inhibit these oxidative reactions which lead to the formation of undesirable products.

The RULER system developed by Robert Kauffman at UDRI was designed to determine the remaining useful life of antioxidants in MIL-L-7808 and MIL-L-23699 oil formulations, hydraulic fluids, stationary equipment oils, etc. More specifically, the method could determine for lubricating oils, the breakdown or decrease in concentration of various types of antioxidants in favor of increasing acid number or peroxide concentration. These observations have significant ramifications to the U.S. Air Force with regard to aviation turbine fuel. This type of testing was applied to aviation fuels, to allow the evaluation of jet fuel quality and antioxidant concentration even after long term storage.

Summary and Results:

New techniques using cyclovoltametry were obtained to measure antioxidant concentration, antioxidant type and oxidation products. The RULER, previously used only on cooking oils and motor oils, had to be modified to be effective with jet fuels. After this modification, the RULER was used to accurately rank the effectiveness of many different types of antioxidants supplied by the Air Force, additive companies and jet fuel producers. In addition, the RULER was successful in measuring many of the oxidation products of fuels including, most notably, peroxides. The ability to measure peroxide

content accurately and with less than 1 milliliter of sample represents a significant improvement over current techniques which are extremely time consuming and use up to 100 milliliters of fuel.

Task: 35
Title: STDS Support
Principal Investigator: Richard Striebich
Affiliation: University of Dayton Research Institute, 300 College Park, Dayton, Ohio 45469
Start/Stop Dates: July 1991 - September 1992

Task Description:

The purpose of this task was to perform a number of modifications on the STDS in order to make the instrument more useful with regard to the thermal stability issues being dealt with currently. The first of these modifications was to install a pyroprobe mechanism to allow the government to examine pyrograms of a deposit which may relate to their ultimate structure or origin. This type of work also required some amount of training of government personnel to operate and maintain this equipment. In addition, the manuals for the STDS were somewhat outdated and this manual required some rewriting.

In addition to these tasks, the STDS required a gas mixer to be installed so that different concentrations of oxygen and nitrogen could be used as reactant gases in the system.

Results and Summary:

The gas mixer was designed, built and delivered to the government. With proper calibration, this mixer can be used to provide any level of oxygen required to conduct gas phase oxidation experiments on the System for Thermal Diagnostic Studies (STDS). The mixer was constructed by building a metal box with digital-flow control valves used to provide a calibrated level of flow through on/off valves to a mixing tee. This particular mixer was made to mix only two gases into one outlet stream.

A CDS pyroprobe was installed and some validation experiments performed to demonstrate that the STDS could be used to subject solid samples to pyrolysis. Small samples of actual deposit from a current Air Force aircraft were obtained and analyzed with this method.

Supplemental manuals for the STDS, developed since the original STDS was completed and delivered, were completed during this time period. These manuals covered mainly the areas of troubleshooting and maintenance of the thermal system. A more complete replacement parts list was provided with the manual.

Task: 36
Title: Chromatography Research and Support
Principal Investigator: Wayne A. Rubey
Affiliation: University of Dayton Research Institute, 300 College Park, Dayton, Ohio 45469-0132
Start/Stop Dates: January 1991 - April 1992

Reports or Technical Information Generated:

W. A. Rubey, An Investigation of Resolution as Encountered in Various Gas Chromatographic Operational Modes, WL-TR-92-2053, in publication, December 1992

Task Description:

Thermal Gradient Programmed Temperature Gas Chromatography (TGPGC) is one of the most recent developments in the field of gas chromatography. This powerful technique, which is very different from conventional techniques, was recently patented by Wayne Rubey of UDRI. This technique is being pursued to increase (by orders of magnitude) chromatographic sensitivity and detection capability, and decrease analysis time from many minutes and sometimes hours, to seconds. The ramifications of the sensitivity increase are significant. The ability to detect trace contaminants may be of paramount importance to the thermal stability issue. However, the ability to reduce analysis times from say, one-half hour to a number of seconds could provide significant benefits to the operational and research Air Force.

There are several specification tests which are based on chromatographic information (or could, in the future be based on chromatographic information) such as simulated distillation. In 1982, the number of lots of JP-4 jet fuel analyzed by specification tests was over 2000 in the continental U.S. alone. Generally, the specification tests are performed both by the refiner and by the Air Force to verify fuel quality. If more specification tests are based on chromatographic information in the future, the ability to conduct tests more quickly and accurately could result in significant savings to the Air Force, its contractors and, therefore, the U.S. taxpayer.

The measurement of dissolved oxygen by gas chromatography is a technique recently developed at UDRI to be used on the Phoenix Rig. The oxygen analysis gas chromatograph, although tested at UDRI, has not been used in conjunction with the on-line system. Funds have been expended for this project and both the Air Force and UDRI anticipate that some training and support may be appropriate for the continued operation of the system recently delivered.

The STDS will be used in a project to investigate the oxidative stability of jet fuels and similar materials under gas phase conditions. The modifications of the STDS for these analyses is not significant but some support will be necessary for the continued operation of the system to obtain high quality data.

Summary and Results:

With regard to Thermal Gradient Programmed Temperature Gas Chromatography (TGPGC), both long and short column sheath assemblies were constructed and tested. Results indicated that successful advances continue to be made in column sheath design and construction. Chromatograms were developed for normal alkane mixtures and other application areas (see Figure 10), which demonstrate the ability of the technique to quickly analyze materials in the same carbon range of jet fuel, and with more sensitivity and resolution than programmed temperature gas chromatography.

The Phoenix Rig uses gas chromatography to conduct analyses of dissolved oxygen levels in thermally stressed jet fuel. The gas chromatograph on this system was malfunctioning and needed some significant modifications. The valves leading to the gas chromatography had been plugged with thermal degradation products of fuel. After disassembly and cleaning, the gas chromatograph was operating as it originally had been.

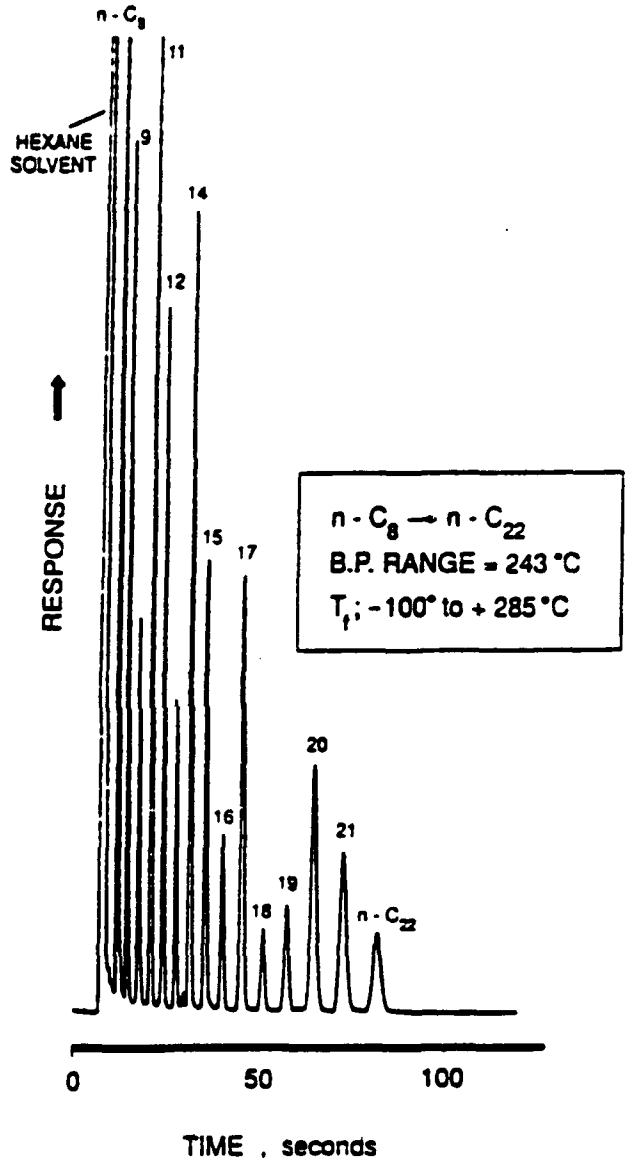


Figure 10. TGPGC of n-Alkane Mixture.

Task: 37

Title: Time-Resolved Molecular Emission Spectrophotometric Technique for Solid Lubrication Analysis

Principal Investigator: Dr. Costy Saba

Affiliation: University of Dayton Research Institute, Wright Patterson Air Force Base

Start/Stop Dates: March 1991 - August 1992

Reports or Technical Information Generated:

Informal Technical Information, BiMonthly Technical Reports

Task Description:

Time-resolved molecular emission spectroscopy (TRMES) is a flame photometric technique that utilizes a cool flame to induce molecular rather than atomic emissions from analytes. Time resolution occurs when two or more analytes in the same sample are induced to the same molecular emission at different rates.

The TRMES method has been used to analyze many different sample types including liquids and solids of both organic and inorganic composition. The primary advantage of TRMES over other analytical techniques is that it can distinguish between different oxidized species in solid inorganic materials that are not amenable to solution chemistry.

This task required modifications to the Perkin-Elmer 5000 Atomic Absorption spectrophotometer located in the WRDC/POSL in-house lubrications laboratory. Modifications were necessary to adapt the instrument for introductions of samples of solid mixtures as well as to obtain flame temperatures low enough to induce only molecular emissions.

This task also required testing and method development for the analyses of solid lubricants, lubricant additives and lubricant thermal and oxidation products. The acquisition of the necessary chemicals, reagents and materials for TRMES analyses was also required.

The finished technique was demonstrated on lubricants or lubricants additives that contain sulfides and have been stressed oxidatively. This demonstration showed the ability of the techniques to determine the presence of different sulfoxy anions that result from the oxidative stressing.

Results and Summary:

A pyrolysis mechanism was used to subject solid lubricants to a flame to provide molecular emissions measurements. This pyrolysis technique was capable of rapid heating and essentially flash volatilize the material into the flame.

Task: 38
Title: Chemometric Analysis of Jet Fuel
Principal Investigator: Dr. Pete Hovey
Affiliation: University of Dayton Research Institute, Dayton, Ohio 45469-0132
Start/Stop Dates: January 1991 - August 1992

Reports or Technical Information Generated:

P. W. Hovey, Chemometric Analyses of Jet-A and JP-4 IR Spectra, UDR-TR-92-119, September 1992

Task Description:

Past studies of jet fuels have used chemometric analysis to investigate the relationship between physical properties and gas chromatographic data; however, the large number of peaks in a jet fuel chromatogram and the narrow range of physical properties in production jet fuels limited the success of the study. Jet fuel IR spectra have fewer peaks and so might be a better candidate for chemometric analysis. The current study was conducted to investigate the relationship between physical properties and IR spectra using chemometric analysis procedures.

There were two specific goals for the Air Force program in chemometric analysis of jet fuel. The first goal was to use chemometrics to provide a method of identifying the specific type of fuel (i.e., JP-4 or JET-A) from IR spectra data. The second goal was to develop a model for predicting physical properties from the IR spectra of a fuel. The same basic chemometric tool, principal components analysis, was instrumental in achieving both goals.

Two types of data were collected for each specimen: 1) physical properties and 2) IR spectra. The physical properties were collected from standard Air Force acceptance tests and the IR spectra were generated in the Fuels Branch, WL/POSF. There were 38 Jet A and 38 JP-4 specimens in the data set.

The physical properties data were compiled into an "Rbase" data base that included approximatelty 30 variables. Although a large number of physical properties are included in the complete acceptance test, only six are collected consistently. The six physical properties used in this study were: total acid number, percent aromatics, specific gravity, freezing point, luminosity number, and flash point. These data were only available for the Jet A specimens.

Summary of Results:

Chemometrics analysis tools were used to investigate the information contained in IR spectra and the relationship between IR spectra and physical properties. The main findings of the investigation were:

- Principal components analysis summarizes the information in the IR spectra into three components
- Clustering is apparent in scatter plots of the principal components
- Hierarchical cluster analysis can be applied to IR spectra to distinguish Jet-A from JP-4
- Some unknown feature is generating sub-clusters within each fuel.
- There are weak correlations between physical properties and the principal components of IR spectra
- Modelling of physical properties may be affected by the sub-clusters.
- Other characterizations of IR spectra, such as moments, may be useful in developing predictive models.

There were no major breakthroughs in the first phase of the investigation. Hierarchical cluster analysis does show a distinct separation between the IR spectra for Jet-A and JP-4 (see Figure 11); however, there is not a strong relationship between physical properties and the principal components. Some evidence indicates that other methods of characterizing IR spectra might prove more useful for predicting physical properties.

Future work should begin with a strong effort to identify the cause of the within fuel clustering. If systematic errors are identified and can be removed, the discrimination between Jet-A and JP-4 might improve and a potential relationship between the physical properties and the principal components might stand out more clearly.

If a specific cause of the clustering is not identified, it may be helpful to normalize the data within each cluster separately before running the principal components analysis. The within-group preprocessing would remove any systematic biases and thus eliminate the apparent clustering. The removal of the within fuel clustering would simplify the stepwise model building.

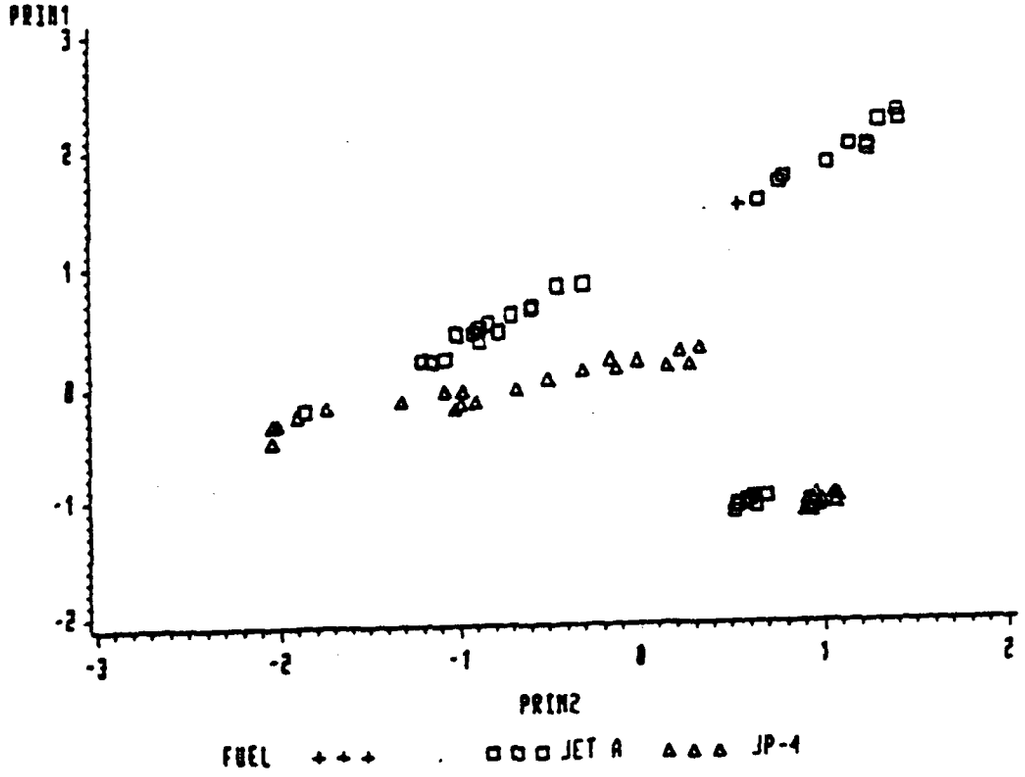


Figure 11. Hierarchical Cluster Analysis.

Other approaches for characterizing IR spectra should also be investigated. The principal components are based on variability in the IR data and may not be directly related to physical properties. Other characterizations, such as the moments, may be more closely related to the physical properties. Data smoothing techniques such as using derivatives of the IR spectra may also be useful in detecting a relationship between the physical properties and the IR spectra.

Task: 39
Title: Evaluation of the Ferroscan
Principal Investigator: Dr. Costy Saba
Affiliation: University of Dayton Research Institute, Wright Patterson Air Force Base, Ohio
Start/Stop Dates: May 1991 - September 1992

Reports or Technical Information Generated:
Bimonthly Interim Letter Reports

Task Description:

Analysis of wear metals has played a significant role in condition monitoring of lubrication systems by improving equipment reliability and reducing maintenance cost. However, current analytical techniques sometimes fail to provide timely data and accurate assessment of wear. Such limitations have encouraged consumers to provide support to develop supplementary diagnostic tools that can provide real time data and improve cost effectiveness. One of the supplementary techniques recently developed is an in-line magnetic wear debris monitor called Ferroscan. Ferroscan is a sensing device for magnetic wear that monitors in real time the concentration and size of particles generated in lubrication systems. Its main objective is to monitor the health of lubricated engine components in order to provide an early warning of impending failure before catastrophic failure occurs.

Summary and Results:

The University of Dayton has evaluated the Ferroscan capability as an in-line wear debris monitor by installing the sensor on an oil test rig. The response and sensitivity of the sensor were determined for various concentrations and sizes of commercial iron powder. The results of this initial testing were encouraging. Excellent sensitivities were obtained for 1 ppm of 0-5 um Fe particles. However, very limited testing was conducted on real used oils. In this program, we focused on determining the sensitivity of the sensor for used oils obtained from normal and abnormal operating gas turbine engines.

Task: 40
Title: Fuel Sheet Disintegration Predictions
Principal Investigator: Dr. R. Tankin
Affiliation: Northwestern University
Start/Stop Dates: December 1991 - May 1992

Reports or Technical Information Generated:
R. Tankin, Fuel Sheet Disintegratin Predictions, Final Report, May 1992

Task Description:

The maximum entropy principle has been successful in predicting the size and velocity distributions for a pressure atomizer operating in an ambient air environment. It is proposed that an attempt be made to extend the maximum entropy principle to a hybrid nozzle configuration. This configuration consists of air assist-pressure atomizer. This study was the intermediate step that will lead to an air blast nozzle. There is no reason to suspect that the maximum entropy principle can not be applied successfully in these situations. The hybrid nozzle in the proposed study was tested over a wide range of flow rates - for both the air and fuel (water).

The proposed research had the following three goals:

1. Operate the hybrid nozzle over a wide range of air and fuel (water) flow rates that are typically prescribed for this nozzle. This nozzle is a pressure atomizer that has swirling air impinging on the spray. The impinging air contributes to the breakup of the spray. The experimental results were compared with those predicted from the maximum entropy principle. To use the maximum entropy principle, estimates had to be made of the source terms, momentum, mass, kinetic energy, and surface energy. These source terms were not empirical constants but were related to the physical aspects of the flow.

2. Operate the nozzle with forced oscillations applied separately to the fuel and air. Determine what effects the forced oscillations had on the size and velocity distributions. Compare the experiments with predictions from maximum entropy.

3. The maximum entropy principle predicts for a particular set of source terms that a bimodal size distribution for the spray exists. This is the first prediction of a bimodal distribution. It was not obvious, in advance, which flow rates will produce the required set of source terms for this nozzle. Therefore, a wide range of flows were scanned in preliminary fashion to determine if a bimodal distribution appeared. If a bimodal distribution appeared, then careful data was taken.

Results and Summary:

A hybrid nozzle is a pressure atomizer that uses air to assist in the atomization of the spray and the patternation. The Allison nozzle, used during the summer of 1991 to determine if a bimodal size distribution could be observed, is a hybrid nozzle. When operated at low flow rates the drops that form just downstream of the breakup region exhibited a bimodal distribution. In the experiments conducted during the period under consideration the effects of the air flow on the size and velocity distributions of the drops were examined (see Figure 12).

Measurements were made just downstream of the liquid sheet breakup region. Using a combination of photographs and droplet distribution measurements, the hybrid spray nozzles were characterized.

Concurrent with these experimental studies, a numerical program was developed at Northwestern University that could model the air flow for this rather complicated geometry. Research of this kind is continuing under other programs.

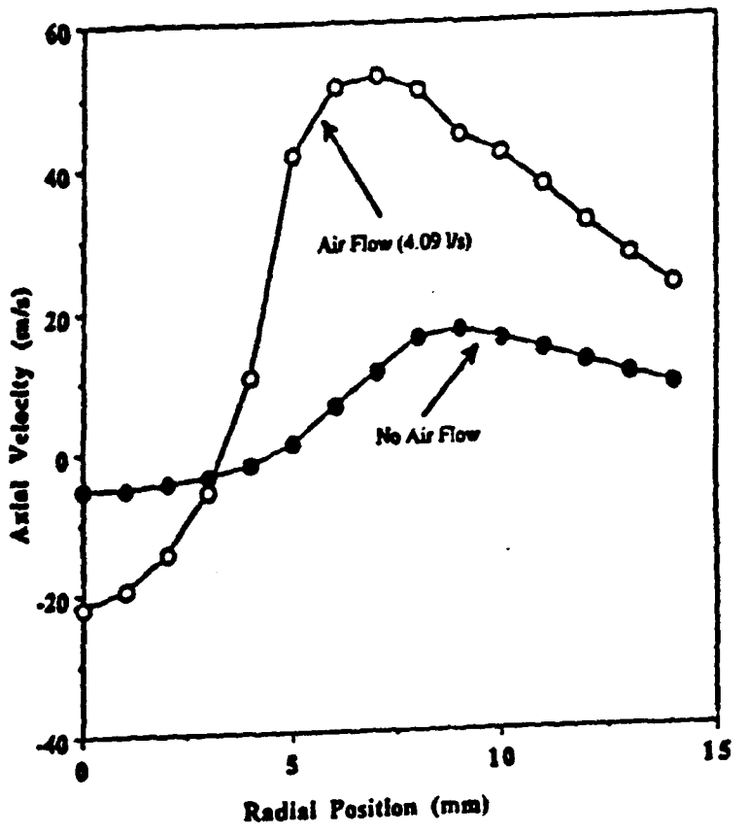


Figure 12. Plots Comparing Axial Velocity Profiles With and Without Air Flow.

Task: 41

Title: High Temperature Lubricant Analysis

Principal Investigator: Wayne Rubey

Affiliation: University Dayton Research Institute, 300 College Park, Dayton, Ohio 45469-0132

Start/Stop Dates: January 1992 - February 1992

Reports or Technical Information Generated:

W. A. Rubey, et al., Modifications of the Lubricants STDS, UDR-TR-92-___, (in publication, February 1992)

Task Description:

The System for Thermal Diagnostic Studies (STDS) is a laboratory system used for conducting thermal decomposition experiments in the gas or liquid phase for liquids, solids or gaseous compounds. The STDS located in the Lubrications Laboratory, Building 490 has been used to investigate the thermal degradation of high temperature lubricants such as the 5-ring polyphenylether (5P4E) as shown below:

The gas phase degradation characteristics of this compound had been investigated under a previous Air Force sponsored program using a University of Dayton STDS. This study demonstrated the feasibility of using the gas phase STDS for investigating this particular compound and other non-conventional and conventional lubricants, thus justifying the purchase of the STDS for the Lubrication Branch.

The STDS had been used in several analyses of high temperature lubricants at WPAFB, using both the mass spectrometer and the Fourier Transform Infrared Detector as detectors for investigating the thermal degradation products of various lubricants, mostly under pyrolytic conditions. After approximately 1-1/2 years of operation, studies directed at the oxidative stability of the 5P4E were unsuccessful in chromatographing the parent compounds (three isomers). It was determined that a thin film chromatographic column, 0.1 um, 0.25 mm internal diameter was required to successfully chromatograph the isomers.

Thus, the purpose of this task was to modify the STDS to chromatograph the oxidative degradation products of the 5P4E lubricant.

Summary of Results:

Bad tailing peaks made us investigate the transfer properties of the GC-MS system. After spending several days making sure that the thermal reaction comparment did not contain any adsorptive

sites, the determination was made that the transfer line to the mass spectrometer was responsible for the poor chromatographic performance. The column was connected to a flame ionization detector in order to verify that the adsorption was inherent in the transfer line. As can be seen, the peak shape and chromatography for 5P4E compounds was excellent, indicating that the mass selective detector transfer line contained adsorptive sites. While inspecting the transfer line, we observed that there were discolorations of the white insulation suggesting a cold spot was present in both the longer and shorter transfer line.

Hewlett Packard provided a new transfer line with an improved design, this time having less adsorption due to higher, more uniform temperatures in the transfer lines. Figure 13 shows the latest chromatogram of the 5P4E in C16 with a series of normal alkanes. Thus, we believe the source of the adsorption has been determined and the corrections to the STDS were made. The column currently on the STDS was the correct column for performing experiments with these types of samples and any type of reactive atmosphere could then be used.

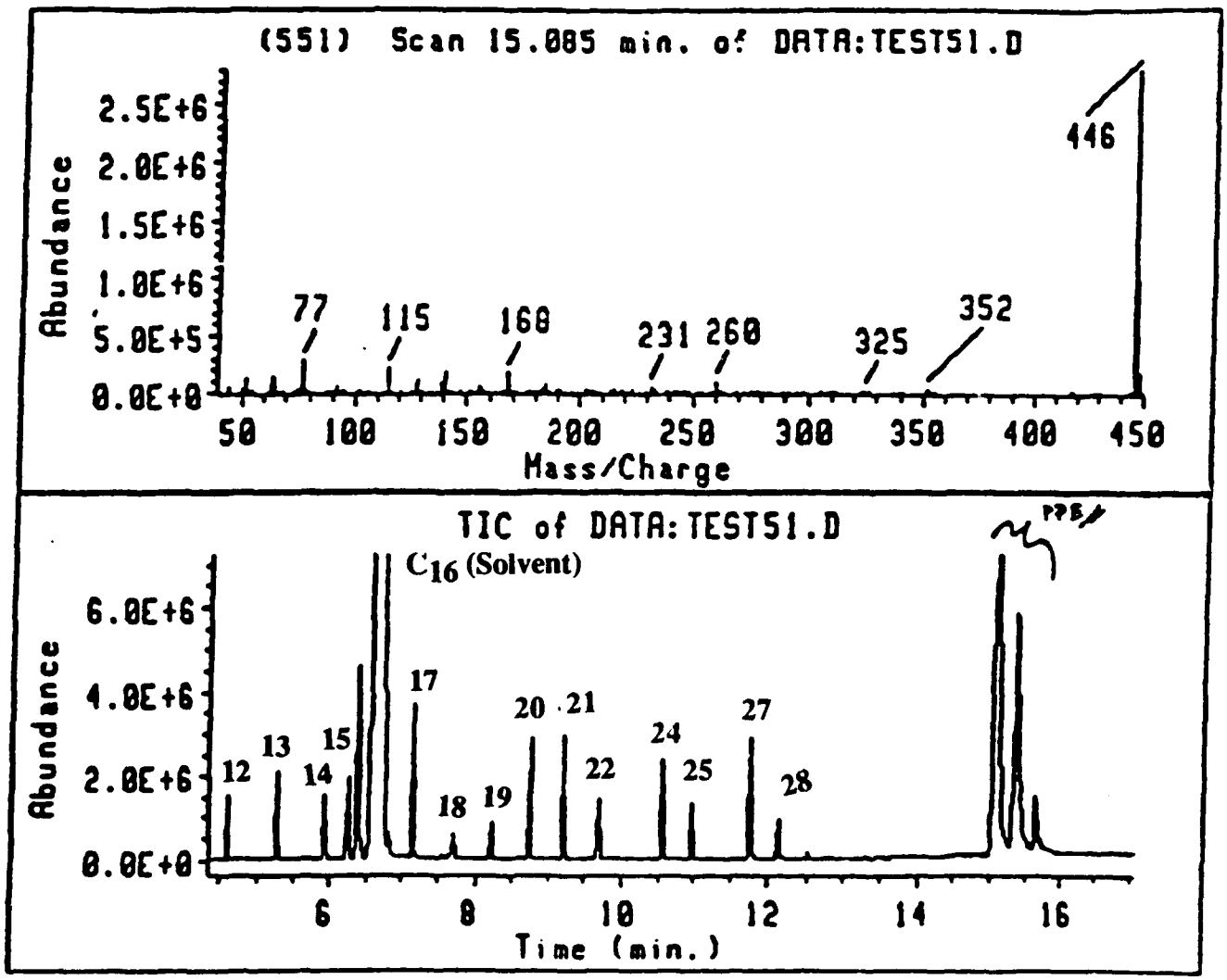


Figure 13. Experiments With New Transfer Line.

Task: 42
Title: Evaluation of a Gas Chromatographic Atomic Emission Detector (AED)
Principal Investigator: M. Keller, C. Saba
Affiliation: University of Dayton Research Institute, Wright Patterson AFB, Ohio
Start/Stop Dates: January 1992 - October 1992

Reports or Technical Information Generated:
Final Letter Report

Task Description:

Analytical characterization of turbine engine lubricants are performed for a number of reasons. For samples received from the field, this may involve characterization of the lubricant basestock or additives as well as the detection and identification of contamination. For experimental and qualification lubricants, the determination of compositional changes in laboratory tested lubricants may aid in the elucidation of their degradation mechanisms.

An HP 5890A gas chromatograph with an HP 5921A atomic emission detector and HP chemstation were used to analyze various lubricants. The GC was equipped with a 25 m x 0.32 mm x 0.17 micron film thickness HP-1 capillary column. Injector, transfer line and detector block temperatures were 280, 320 and 320°C, respectively. The oven was programmed 40 to 310°C at 15°C/minute, final hold 15 minutes. Lubricants analyzed included a MIL-L-7808 lubricant, and three experimental high temperature lubricants, including a fresh polyphenyl ether and corrosion and oxidation tested polyphenyl thioether and cyclotriphosphazene.

Summary of Results:

a. MIL-L-7808 Turbine Engine Lubricants

These type lubricants consist of mixtures of synthetic esters with various additive packages. Usually, these lubricants are formulated with secondary amine antioxidants (phenothiazine, PANA, octyl-PANA or DODPA) and an antiwear additive (usually tricresylphosphate (TCP)). A typical GC-AED analyses might consist of fingerprinting or comparison of basestocks (esters) and additive packages.

A typical three-channel chromatograph shows the diverse components that exist in a typical turbine engine lubricant (Figure 1). The nitrogen and phosphorous channel chromatograms display the differences in sensitivity and selectivity between the two channels. The minimumn detectable level is approximately 1 pg/sec for phosphorous-178 and 50 pg/sec for nitrogen-174. Also, carbon tends to cause interference due to its high sensitivity and large concentration in organic compounds. The reported selectivity over carbon is 5000 for phosphorous-178 and 2000 for nitrogen-174. As a result, the chromatograms show that the phosphorous compound (TCP) is easily detectable above the carbon

basestock (Figure 14), while the aromatic amines (PANA and DODPA) are not, despite simular elemental concentrations for both N and P in the lubricant.

Unwanted hydrocarbon response can be minimized using a software feature that utilizes background suppression. By selecting a major hydrocarbon peak in the chromatogram that does not contain the desired element, either one internal to the sample or one added to the sample, a more element selective chromatogram can be developed. In general, the presence of an element in a particular compound is indicated by a relatively large response for the compound at that elements monitoring wavelength. However, the most certain way to confirm the presence of an element is by the use of spectral snapshots. This software feature allows for the display of the spectrum at any particular elution time in the chromatogram. From this spectrum, the presence of the element in question is confirmed by the presence of that elements characteristic emission wavelengths. Because of the very large memory requirements, snapshots are only available over a limited wavelength range (about 70 nm) for the most recent analysis.

In addition to MIL-L-7808 lubes, high temperature lubes of several varieties were investigated.

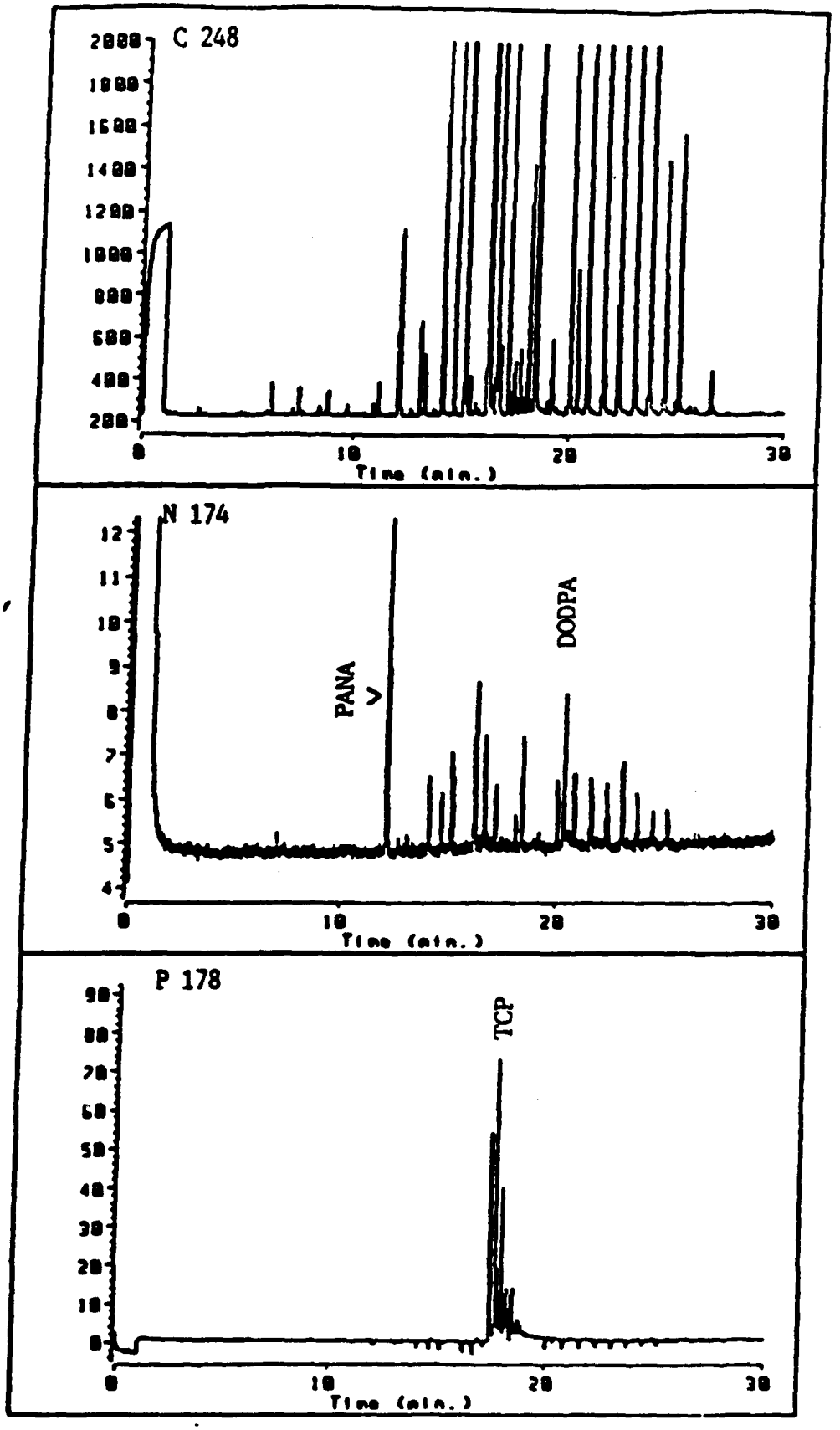


Figure 14. Three Element Chromatogram of a Fresh MIL-L-7808 Lubricant.

SECTION 4 - LIST OF REPORTS GENERATED UNDER THIS EFFORT

S.L. Mazer, Customized GC-MS Training: Course Notes (Task 1)

S. L. Mazer, Mass Spectral Interpretation: Course Notes (Task 1)

W. A. Rubey, et al. STDS-Description & Operation, UDR-DR-89-15 (Task 2)

W. A. Rubey, et al. STDS Tubular Gas Flow Reactor: Description & Operation, UDR-DR-89-16 (Task 2)

R. C. Striebich, et al. STDS Supplemental Manal for STDS, UDR-TR-92 (Task 2)

R. C. Striebich, et al., Low Pressure Catalytic Test Cell Assembly, UDR-TR-91-99 (Task 3)

McCoy, Studies on the Mechanism of Olefin Metathesis Promoted by a Rhenium Oxide Alumina Catalyst, Ph.D. Dissertation, January 1991 (Task 3)

C. S. Saba, Alternate Spectrometric Oil Analysis Techniques, UDR-TR-91-156, December, 1991 (Task 4)

R. C. Striebich, et at., A Condensed Phase Test Cell Assembly for the STDS, WL-TR-92-2040 (Task 5)

L. Krishnamurthy, Sensitivity Equation Development for the K-E Turbulence Model, UDR-TR-89-36, May 1989 (Task 7)

C. S. Saba, Determination of the Shelf-Life of Oil Calibration Standards for the Perkin-Elmer P.W.M.A., UDR-NM-MO-92-07, October 1992 (Task 13)

R. Becker, et al., Elective Field Measurements in Flames, Final Report (Task 17)

L. Hall, RJ-7 High Density Fuel Development, Final Report on Task 20, Sun Refining & Marketing Company, October 1990.

Carillo, Development of a High Resolution CARS System for Use in the Study of Electrical Discharges in Nitrogen, July 1990, Masters Thesis (Task 20)

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W. Schulz, Development of a Thermal Oxidative Stress Test for Elucidating Fuel Chemistry and Determining Additive Efficiencies, Final Report, July 1991.

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R. Tankin, An Experimental Study of Hybrid Nozzles, September 1992

D. S. Marcum, Alkali Plasma Diagnostics, Final Report, September 1992.

B. Goplen, Energy Deposition in a VKP 7555S Collector, MRC/WDC-R-272, September 1990.

B. Kumar, Polymeric Materials for Battery Applications, UDR-TR-90-96, WRDC-TR-90, October 1990.

R. Kauffman, et al., Data Acquisition System, UDR-TR-92-130, December 1992.

R. Kauffman, et al., New Techniques to Predict and Evaluate the Effectiveness of Antioxidants in Jet Fuel,

ACS Presentation/Proceedings, April 1992.

R. Kauffman, Antioxidant Effectiveness of Jet Fuel Additives Using the RULER, UDR-TR-92-148.

W. A. Rubey, An Investigation of Resolution as Encountered in Various GC Operational Modes, WL-TR-92-__, in publication, December 1992.

W. A. Rubey, Reva Del Garda paper.

P. W.Hovey, Chemometric Analysis of Jet A and JP-4 IR Spectra, UDR-TR-92-119.

R. Tankin, Fuel Sheet Disintegration Predictions, Final Report, May 1992.

W. A. Rubey, Modifications of the Lubrications STDS, UDR-TR-in publication, February 1992.

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SUPPLEMENTARY

INFORMATION

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COMMENTS:

Re: Scholarly Report - missing page 26

We apologize but there is no page 26. We miss numbered - page 27 should be 26 etc.

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